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VINYLPHENYL KETONE AND SOME OF ITS HOMOLOGUES.

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While studying the reaction between unsaturated ketones and organic magnesium compounds it was desirable to compare the behavior of benzalacetone with that of vinylphenyl ketone and its homologues. An examination of the literature showed that very few of the latter had been prepared. Moureu,[1] in the course of an admirable investigation of acrylic acid, allowed the chloride to react with benzene in the presence of aluminium chloride and obtained a very small yield of a colorless solid that he regarded as vinylphenyl ketone. This conclusion was not accepted by Klages,[2] who treated α-brompropiophenone and its homologues with alcoholic potassium hydroxide and obtained yellow liquids which he assumed to be the first members of this class of ketones.

In a recent paper[3] I showed that the yellow liquids described by Klages are mixtures that do not contain a trace of unsaturated compounds. This leaves the vinylphenyl ketone of

[1] Ann. Chim. Phys., [7] **2**, 198.
[2] Chem. Ztg., **1908**, 318.
[3] THIS JOURNAL, **41**, 417.

Moureu as the only possible representative of this type of unsaturated ketone. Moureu adduced no direct evidence that his product was unsaturated. As described by him the substance seemed much too stable and unreactive to be a vinyl derivative. It was necessary, therefore, to repeat Moureu's experiment in spite of the difficulty of getting the materials and the discouragingly small yield of less than 4 per cent.

I found that the solid described by Moureu is not vinylphenyl ketone but the isomeric saturated cyclic compound, α-hydrindone. This is, doubtless, formed from vinylphenyl ketone, either by direct condensation or, more probably, by preliminary addition of hydrogen chloride to the unsaturated ketone and subsequent ring formation:

$$\text{I. } CH_2{:}CHCOCl + C_6H_6 = CH_2{:}CHCOC_6H_5 + HCl.$$

$$\text{II. } CH_2{:}CHCOC_6H_5 + HCl = CH_2ClCH_2COC_6H_5.$$

$$\text{III. } CH_2ClCH_2COC_6H_5 = C_6H_4\begin{cases}CH_2\\ CO\end{cases}CH_2 + HCl.$$

As both vinylphenyl ketone and β-chlorpropiophenone give α-hydrindone when brought in contact with aluminium chloride, it is not possible to decide between these reactions, but the halogen compound gives a much larger yield than the unsaturated ketone.

The formation of hydrindone from vinylphenyl ketone illustrates the reactivity which makes the preparation of this substance a difficult undertaking. After a number of unsuccessful attempts a possible, though far from satisfactory, method of preparation was found. This depends on the removal of bromine from α,β-dibrompropiophenone. The dibrom ketone was easily made in any desired quantity from dibrompropionyl chloride and benzene by the Friedel and Crafts reaction. The elimination of bromine proved more difficult. Zinc and alcohol gave only propiophenone and α,δ-dibenzoylbutane—obviously reduction products of the unsaturated ketone. The combination of zinc and acetone recently recommended by Straus[1] for cases in which easily reducible substances are to be expected proved equally value-

[1] Ann. Chem. (Liebig), **342**, 190.

less. The removal of halogen took place very slowly and the resulting unsaturated ketone was contaminated with such quantities of condensation products, formed by the prolonged action of zinc bromide on boiling acetone, that it was impossible to isolate a pure product.

A more satisfactory reagent was found in potassium iodide. Völker and Zolla[1] found as early as 1878 that this substance can be used for getting acrylic acid from α,β-dibrompropionic acid. Since then the reaction between potassium iodide and polyhalogen compounds that have two halogen atoms in combination with adjoining carbon atoms has been the subject of several special investigations but has found little use for the preparation of unsaturated compounds. This is due, doubtless, to the fact that in the cases studied the reaction took place very slowly and ultimately resulted in a condition of equilibrium. This is not true in the case of α,β-dibrom ketones. Preliminary experiments with benzalacetone dibromide and benzalacetophenone dibromide showed that potassium iodide dissolved in alcohol is an admirable reagent for eliminating bromine from this type of dihalogen compound; the reaction proceeded rapidly, was complete, and yielded the calculated quantity of unsaturated ketone.

That the reaction between potassium iodide and α,β-dibrompropiophenone is not so satisfactory is due solely to the reactivity of vinylphenyl ketone. In the presence of minute quantities of acid this is capable of combining with the alcohol used as medium. The product is, therefore, always a mixture of the unsaturated ketone and β-alkoxypropiophenone. This can be separated by repeated fractional distillation under diminished pressure, but the yield of unsaturated ketone is variable—from 25 to 60 per cent. of the calculated quantity. As I found no other satisfactory medium and no means of removing alcohol from ethoxypropiophenone, this was the best yield obtained.

Vinylphenyl ketone is, as was to be expected, the most reactive of all α,β-unsaturated ketones with the possible exception of the vinylalkyl ketones recently made by Blaise and Maire.[2]

[1] Ann. Chem. (Liebig); **192**, 102.
[2] Compt. Rend., **142**, 215.

It instantaneously reduces permanganate solutions, combines energetically with bromine, halogen acids, and primary and secondary amines, and polymerizes both when exposed to sunlight and when heated to comparatively low temperatures. The pure ketone apparently undergoes no change when boiled with pure alcohol but if a drop of aqueous hydrochloric acid be added to the liquid or if the ketone contain any impurity that, like β-chlorpropiophenone, can react with alcohol to give a halogen acid, it adds alcohol more or less rapidly and passes into β-ethoxypropiophenone.

The ketone also combines readily with acid sulphites. The product with hydrogen sodium sulphite is a very soluble sodium salt of β-benzoylethanesulphonic acid that is not affected by boiling with a solution of sodium carbonate. This explains why none of the ketone was obtained by Moureu. Experiments made after the properties of the ketone were known showed that the crude product of the reaction between the chloride of acrylic acid and benzene contains variable amounts of the unsaturated ketone. Much of this is destroyed during the process of distillation, the remainder being lost by the subsequent treatment with acid sodium sulphite adopted by Moureu.

The reactions that ultimately yielded pure vinylphenyl ketone were also used for making propenylphenyl ketone and isobutenylphenyl ketone. These ketones are far less reactive than the first member of the series. They do not readily combine with alcohol and they show no tendency towards polymerization during distillation under diminished pressure. Their preparation by this method therefore presented no difficulties and the yields were satisfactory. Most of the homologues that have alkyl in place of hydrogen in the β position are, however, probably obtained more easily by the Friedel and Crafts reaction. This was tried with crotonyl chloride and benzene, and gave excellent results. The yield of propenylphenyl ketone was 90 per cent. of the calculated amount. The only other product obtained was β-phenylbutyrophenone. The formation of this substance under these conditions is interesting because it indicates that benzene and

aluminium chloride may react exactly like organic magnesium compounds with unsaturated ketones:

I. $CH_3CH:CHCOC_6H_5 + C_6H_6 + AlCl_3 = C_6H_5CH(CH_3)CH:C(OAlCl_2)C_6H_5$.

II. $C_6H_5CH(CH_3)CH:C(OAlCl_2)C_6H_5 + H_2O = C_6H_5CH(CH_3)CH:C(OH)C_6H_5 \longrightarrow C_6H_5CH(CH_3)CH_2COC_6H_5$.

The effect of the methyl groups in the β position is shown most clearly by the behavior of these ketones towards phenylhydrazine and towards organic magnesium compounds. When an alcoholic solution of phenylhydrazine containing a few drops of acetic acid is added to a solution of vinylphenyl ketone in the same solvent, the liquid immediately becomes hot and in a few minutes all of the ketone is transformed into a pyrazoline derivative:

$$CH_2:CHCOC_6H_5 + C_6H_5NHNH_2 = \begin{array}{l} CH_2CH_2 \\ | \quad \diagdown \\ C_6H_5N—N \end{array} \begin{array}{l} \\ \diagup CC_6H_5 \\ \\ \end{array} + H_2O$$

With propenylphenyl ketone there is no evidence of reaction at the ordinary temperature, but the corresponding pyrazoline is obtained when the mixture is boiled:

$$CH_3CH:CHCOC_6H_5 + C_6H_5NHNH_2 = \begin{array}{l} CH_3CHCH_2 \\ | \quad \diagdown \\ C_6H_5N—N \end{array} \begin{array}{l} \\ \diagup CC_6H_5 \\ \\ \end{array} + H_2O$$

Isobutylphenyl ketone forms no pyrazoline derivative under these conditions:

$$(CH_3)_2C:CHCOC_6H_5 + C_6H_5NHNH_2 = (CH_3)_2C:CHC(C_6H_5):NNHC_6H_5 + H_2O$$

The behavior of the ketones towards organic magnesium compounds is shown in the following table, in which they are grouped with a few of the most closely related compounds studied in earlier investigations. The numbers represent, in per cents., the relative amounts of 1,4-addition product formed:

Unsaturated compound.	Reagent. C_2H_5MgBr.	Reagent. C_6H_5MgBr.
$CH_2:CHCHO$	0	0
$CH_2:CHCOC_6H_5$	100	100
$CH_3CH:CHCOCH_3$	75	40
$CH_3CH:CHCOC_6H_5$	100	100
$C_6H_5CH:CHCOCH_3$	60	12
$C_6H_5CH:CHCOC_6H_5$	99	94
$(CH_3)_2C:CHCOCH_3$	0	0
$(CH_3)_2C:CHCOC_6H_5$	...	95
$(C_6H_5)_2C:CHCOC_6H_5$	18	0

EXPERIMENTAL PART.

I. Repetition of the Experiments of Moureu.

The large quantity of acrylic acid needed for these experiments was made by the method proposed by Moureu and I am able to confirm his statements that this procedure gives a perfectly pure acid. The chloride was obtained by treating the sodium salt with phosphorus oxychloride, but I found the addition of high-boiling paraffine oil, recommended by Moureu, both unnecessary and disadvantageous. When the sodium salt is dried slowly it is left as a porous powder that affords excellent contact and all that is necessary to insure a good yield of the chloride is sufficiently slow addition of the oxychloride. In the absence of paraffine oil a single redistillation of the product gives over 90 per cent. of the possible amount of pure chloride.

The reaction with benzene and aluminium chloride was carried out as directed by Moureu, and the product isolated by his method of procedure. The yield of pure solid, melting at 41°–42°, was 12 grams from 250 grams of chloride.

The results of an analysis and a molecular weight determination agreed with those published by Moureu, but a test with potassium permanganate dissolved in acetone showed at once that the substance could not be an α,β-unsaturated ketone, because its effect on permanganate did not exceed that of acetone. As α-hydrindone is described as a colorless solid melting at 40° and forming an unstable phenylhydrazone melting at 130°—the properties of the phenylhydrazone obtained by Moureu—there seemed little room for doubt as

to the nature of the substance. α-Hydrindone was made from phenylpropionyl chloride and the melting point of a mixture of the substances compared with that of the components; all melted at the same temperature. Moureu's vinylphenyl ketone is, therefore, α-hydrindone.

II. Vinylphenyl Ketone.

The necessity of making large quantities of pure dibrompropionic acid led to a considerable improvement in the method of preparation. The addition of bromine to allyl alcohol was carried out in carbon bisulphide, but by cooling in a freezing mixture it was possible to use a much smaller quantity of solvent than was recommended by Michael and Norton[1] and to add the bromine much more rapidly without diminishing the yield. Thirteen hundred and sixty grams of dry bromine were diluted with an equal volume of carbon bisulphide and added, in less than 2 hours, to 500 grams of allyl alcohol dissolved in 2 liters of the same solvent. The bromine was delivered from dropping funnels into the alcohol contained in two flasks that were shaken in freezing mixtures. The solvent was removed by distillation as soon as a decided color of bromine remained after shaking for 10 minutes. The residue, fractioned under diminished pressure, gave 1690 grams of dibrompropyl alcohol boiling at 115°–120° (18 mm.), a yield of 91 per cent.

The mixture of concentrated and fuming nitric acid proposed by Tollens and Caspary[2] was used for oxidizing the alcohol to dibrompropionic acid. To avoid the sudden, energetic reaction that takes place soon after the nitric acid is added, the mixture was kept in ice water for a few hours, then overnight at the ordinary temperature. In this way it was possible to oxidize in quantities of 250 grams without loss of material. Most of the water and acid was removed, as usual, by distillation under atmospheric pressure, the remainder by heating in boiling water under greatly diminished pressure.

It has long been known that a good yield of impure dibrom-

[1] This Journal, **2**, 18.
[2] Ann. Chem. (Liebig), **167**, 225.

propionic acid can be obtained by oxidation of dibrompropyl alcohol, but that the method of purification devised by Tollens and Munder[1] involves serious loss. Most of this can be avoided by distillation under diminished pressure. When the crude acid is heated under a pressure of 20 mm. it first yields a small quantity of low-boiling distillate, then suddenly turns red and begins to evolve oxides of nitrogen, carbon monoxide, and carbon dioxide when the temperature reaches 135°–140°. The residue left after the evolution of gases ceases is almost colorless. It begins to distil at 150° (20 mm.) and the fraction collected at 150°–160° is sufficiently pure for most purposes, but contains small quantities of nitric acid derivatives and some polymeric product. On redistillation it yields a small quantity of nitric acid and leaves a residue of non-volatile material. The fraction collected at 155°–158° boils constantly, when distilled again, at 160° (20 mm.)—the boiling point of pure α,β-dibrompropionic acid. The yield was 1387 grams of pure acid from 1690 grams of dibrompropyl alcohol—76 per cent. of the calculated amount.

Dibrompropionic acid reacts very slowly with phosphorus trichloride and it is necessary to heat for 12 hours to complete the reaction. The acid chloride was easily obtained, however, by suspending the acid in a small quantity of phosphorus oxychloride, cooling the mixture in ice water, and adding the calculated quantity of phosphorus pentachloride in small quantities. The resulting liquid was fractioned under diminished pressure. A considerable quantity of the chloride distils with the oxychloride, but this is easily recovered by removing most of the oxychloride from this fraction by distillation under ordinary pressure and then redistilling the remainder under diminished pressure. The properties of the chloride were the same as those found by Moureu in a product obtained by adding bromine to the chloride of acrylic acid.

Dibrompropiophenone, $CH_2BrCHBrCOC_6H_5$.—To prepare this ketone 250 grams of dibrompropionyl chloride and 100 grams of benzene were dissolved in 500 cc. of carbon bisulphide and the solution cooled in a freezing mixture. Ground aluminium

[1] Ann. Chem. (Liebig), **167**, 240.

chloride was then added, in 10–20 gram quantities, until further addition no longer produced rapid evolution of hydrogen chloride—150 to 160 grams. The reaction is a remarkably clean one, because a colorless aluminium derivative of the ketone separates from the liquid and thus escapes further change. The product was immediately poured into a mixture of ice and concentrated hydrochloric acid, the carbon bisulphide layer drawn into a shallow dish, and the solvent allowed to evaporate. This left a colorless solid and a small quantity of a pale yellow oil. The oil was removed with a pump, the solid washed thoroughly—first with water, then with small quantities of absolute alcohol—and purified by crystallization from alcohol or low-boiling ligroin. The yield was excellent: 250 grams of chloride gave 290 grams of crude and 278 grams of pure ketone—95 per cent. of the calculated amount.

Analysis:

0.1525 gram substance gave 0.2047 gram CO_2 and 0.0411 gram H_2O.

	Calculated for $C_9H_8OBr_2$.	Found.
C	36.9	36.6
H	2.7	3.0

α,β-Dibrompropiophenone crystallizes in large needles or plates melting at 58°. It is readily soluble in ether, acetone, and boiling alcohol, moderately in cold alcohol and ligroin.

Reaction with Zinc.—For the purpose of eliminating bromine, a little more than the calculated quantity of zinc dust was added in small quantities to a solution of 100 grams of the bromketone in 500 cc. of alcohol. After boiling for an hour most of the alcohol was removed by distillation and the residue poured into water. This precipitated an oil that partially solidified on standing. The solid was removed and a small quantity tested with bromine in a freezing mixture, but no unsaturated ketone was found. The oil was, therefore, dried and distilled under diminished pressure. The distillate was pure propiophenone, identified by its boiling point and the melting point of its oxime.

The solid that separated when the alcoholic residue was poured into water was purified by crystallization from a mixture of chloroform and alcohol. It separated in small prisms that melted at 112°.

Analysis:

0.1295 gram substance gave 0.3816 gram CO_2 and 0.0815 gram H_2O.

	Calculated for $C_{18}H_{18}O_2$.	Found.
C	81.2	81.4
H	6.7	7.0

The molecular weight was determined in carbon tetrachloride ($k = 48$).

Solvent. Grams.	Substance. Gram.	Elevation of boiling point.	Molecular weight.
56.1	0.3210	0.090	282
56.1	0.5305	0.147	309
56.1	0.7510	0.220	292
Calculated for $C_{18}H_{18}O_2$,			266

When boiled with an alcoholic solution of hydroxylamine hydrochloride and an excess of potassium hydroxide, the substance gave a very sparingly soluble dioxime. This was purified by recrystallization from amyl alcohol, from which it separated in minute needles melting at 232°.

Analysis:

0.1431 gram substance gave 0.3815 gram CO_2 and 0.0884 gram H_2O.

	Calculated for $C_{18}H_{20}O_2N_2$.	Found.
C	73.0	72.7
H	6.7	6.8

Eight grams of the dioxime were treated with phosphorus pentachloride in absolute ether, the product boiled with water, and the resulting solid heated at 160° with concentrated hydrochloric acid for 8 hours. From the acid solution ether extracted 1.8 grams of an acid that melted at 149° after one crystallization from water.

Analysis:

0.2011 gram substance gave 0.3627 gram CO_2 and 0.1285 gram H_2O.

	Calculated for $C_6H_{10}O_4$.	Found.
C	49.3	49.2
H	6.9	7.2

The substance is adipic acid. The solid melting at 112° is, therefore, dibenzoylbutane, a dimolecular reduction product of vinylphenyl ketone:

$$2CH_2:CHCOC_6H_5 + 2H = \begin{matrix} CH_2CH_2COC_6H_5 \\ | \\ CH_2CH_2COC_6H_5 \end{matrix}.$$

This ketone was made by Étaix[1] from the chloride of adipic acid and benzene, by the Friedel and Crafts reaction. Étaix gives 102° as the melting point of the ketone and 218° as the melting point of the oxime, but he evidently did not have pure substances, as his ketone was colored and he made no attempt to purify the oxime.

The formation of these two reduction products of vinylphenyl ketone—propiophenone and dibenzoylbutane—in the presence of a large quantity of unchanged dibromketone, showed that it was hopeless to attempt to remove the bromine with metals in the presence of alcohol. Acetone was therefore substituted for alcohol as the solvent. In acetone the zinc disappears very slowly; it was necessary to boil for 8 hours to get a product fairly free from bromine. This product undoubtedly contained some unsaturated ketone, since it was possible, by vacuum distillation, to separate a fraction that was free from bromine and that gave α,β-dibrompropiophenone when treated with bromine in a freezing mixture. The amount of vinylphenyl ketone present was, however, relatively small and it was impossible to free it from the numerous condensation products of acetone with which it was mixed.

Reaction with Potassium Iodide.—In a flask connected with an inverted condenser 120 grams of powdered potassium iodide were partially dissolved in 500 cc. of boiling alcohol.

[1] Ann. Chim. Phys., [7] **9**, 372.

To this solution 100 grams of the bromketone were added in small portions. The mixture was boiled for two hours, then cooled and poured into a solution containing an excess of sodium thiosulphate. The solution was extracted with ether, the ethereal solution dried with fused sodium sulphate, and the alcohol and ether removed by distillation. The residue—a yellow liquid that did not solidify in a freezing mixture—was distilled under diminished pressure. It gave a colorless distillate boiling at 105°–135° (18 mm.). A test with bromine showed that nearly half of this distillate was vinylphenyl ketone. The experiment was, therefore, repeated in order to accumulate sufficient material with which to undertake a separation. Five hundred grams of dibrompropiophenone gave 208 grams of this colorless liquid. By repeated fractional distillation under diminished pressure, two pure substances were finally obtained from it.

Vinylphenyl Ketone, $CH_2 : CHCOC_6H_5$.—The unsaturated ketone accumulated in the lower-boiling fractions. When perfectly pure it boiled constantly at 115° (18 mm.). The purity was established by analysis and by a test with bromine which, in this case, is more conclusive than the results of analyses.

Analysis:

0.1340 gram substance gave 0.4009 gram CO_2 and 0.0729 gram H_2O.

	Calculated for C_9H_8O.	Found.
C	81.8	81.6
H	6.1	6.0

The molecular weight was determined in benzene ($k = 50$).

Solvent. Grams.	Substance. Gram.	Depression of freezing point.	Molecular weight.
12.0	0.1640	0.500	137
12.0	0.2205	0.634	145
12.0	0.3500	1.086	134
Calculated for C_9H_8O,			132

In order to test the purity of the substance, 2 grams were dissolved in freshly distilled carbon bisulphide, and the solution cooled in a freezing mixture and treated with a solution of pure,

dry bromine in the same solvent until a faint color of bromine appeared in the liquid. When the solvent was evaporated under diminished pressure it left pure dibrompropiophenone. The liquid boiling at 115° (18 mm.) was, therefore, pure vinylphenyl ketone. The yield was 78 grams from 500 grams of dibrompropiophenone.

Vinylphenyl ketone is an unstable substance. When kept in sealed tubes in the dark it changes very slowly, but ultimately becomes discolored and viscous. The same or a similar change takes place much more rapidly in the light, and when the substance is exposed to light and air the change is accompanied by oxidation with formation of formaldehyde as one of the products. A small quantity of nonvolatile matter is left after each distillation under diminished pressure and when the ketone is kept at 115°—the boiling point under a pressure of 18 mm.—it soon becomes yellow. When heated rapidly in a bath under atmospheric pressure it begins to change perceptibly at 120°, then suddenly boils and decomposes when the temperature of the bath reaches 150°–160°, the heat evolved being sufficient to raise the temperature of the substance above 200°. A similar sudden transformation occasionally takes place when the ketone is exposed to direct sunlight.

Diphenylpyrazoline, $C_{15}H_{14}N_2$.—Vinylphenyl ketone reacts energetically with phenylhydrazine. Three grams of the ketone were poured into a solution of an equal weight of the base in 10 cc. of alcohol, to which a few drops of glacial acetic acid had been added. The liquid immediately became hot and in a very short time most of the product had separated in crystalline form. It was washed with alcohol and recrystallized from absolute alcohol. It separates in large yellow needles, melting at 158°. It is sparingly soluble in alcohol and ether.

Analysis:

0.1572 gram substance gave 0.4700 gram CO_2 and 0.0915 gram H_2O.

	Calculated for $C_{15}H_{14}N_2$.	Found.
C	81.1	81.5
H	6.3	6.5

As vinylphenyl ketone combines energetically with primary amines, this substance may be either 1,3-diphenylpyrazoline, formed from the hydrazone,

$$\begin{matrix} CH_2 : CHCC_6H_5 \\ \| \\ C_6H_5NH.N \end{matrix} = \begin{matrix} CH_2CH_2 \\ | \quad \diagdown \\ C_6H_5N-N \end{matrix} \!\!> CC_6H_5,$$

or 1,5-diphenylpyrazoline formed from an addition product,

$$C_6H_5NHNHCH_2CH_2COC_6H_5 = \begin{matrix} CH_2CH_2 \\ | \quad \diagdown \\ N=N-C_6H_5 \end{matrix} \!\!> CC_6H_5 + H_2O.$$

By analogy with the product obtained from crotonic aldehyde the former would be expected, but as the aldehyde contains a much more reactive carbonyl group than the ketone, this method of reasoning is not conclusive.

Ethoxypropiophenone, $C_2H_5OCH_2CH_2COC_6H_5$.—This substance was the second product of the reaction between potassium iodide and dibrompropiophenone, in alcoholic solution. It is easily made by dissolving vinylphenyl ketone in alcohol, adding a few drops of hydrochloric acid, and boiling for a short time, and also by boiling β-chlorpropiophenone with alcoholic potassium hydroxide. It is a colorless liquid that boils at 135° (18 mm.), solidifies in a freezing mixture, and then melts at about 12°.

Analysis:

0.1421 gram substance gave 0.3883 gram CO_2 and 0.1023 gram H_2O.

	Calculated for $C_{11}H_{14}O_2$.	Found.
C	74.2	74.5
H	7.8	8.0

Ethoxypropiophenone phenylhydrazone was made by boiling the ketone with phenylhydrazine in alcoholic solution and recrystallizing the product from methyl alcohol. It crystallizes in very pale yellow plates that melt at 86°. It is readily soluble in alcohol and ether, moderately in methyl alcohol and ligroin.

Analysis:

0.1580 gram substance gave 0.4428 gram CO_2 and 0.1070 gram H_2O.

	Calculated for $C_{17}H_{20}ON_2$.	Found.
C	76.1	76.4
H	7.5	7.5

β-Chlorpropiophenone, $ClCH_2CH_2COC_6H_5$.—Vinylphenyl ketone absorbs gaseous hydrogen chloride and forms β-chlorpropiophenone. A pure product is obtained by saturating a cooled solution of the ketone in absolute ether with hydrogen chloride and allowing the solvent to evaporate. It is a colorless solid that crystallizes in large plates, melting at 57°. It is readily soluble in all common organic solvents except low-boiling ligroin.

Analysis:

0.1991 gram substance gave 0.4672 gram CO_2 and 0.0927 gram H_2O.

	Calculated for C_9H_9OCl.	Found.
C	64.1	64.0
H	5.3	5.2

When the chlorketone is heated under diminished pressure (20 mm.) it begins to lose hydrogen chloride and distil freely at about 120°. About 25 per cent. of the material is left as a brown, nonvolatile residue. The distillate is composed of variable quantities of unchanged substance and vinylphenyl ketone.

Sodium Benzoylethanesulphonate, $C_6H_5COCH_2CH_2SO_3Na.H_2O$.—Vinylphenyl ketone combines readily with acid sulphites. When the pure ketone was warmed with a saturated solution containing slightly more than the calculated quantity of sodium hydrogen sulphite, a rapid reaction commenced at 50°, the oily ketone dissolving in a few minutes while the temperature rose to the boiling point of the solution. On cooling the liquid, the addition product separated in large colorless plates. The salt is readily soluble in water. It crystallizes with one molecule of water, which it loses below 100°.

Analysis:

I. 0.2297 gram salt lost 0.0158 gram at 120° and the residue gave 0.0649 gram Na_2SO_4.

II. 0.2322 gram salt lost 0.0162 gram at 120° and the residue gave 0.0640 gram Na_2SO_4.

	Calculated for $C_8H_9O_4SNa.H_2O$.	Found. I.	II.
H_2O	7.09	6.86	6.97
Na	9.74	9.75	9.60

The sodium salt is not decomposed either by sodium carbonate or by dilute acids.

β-Benzoylethanesulphonic Acid, $C_6H_5COCH_2CH_2SO_3H$.—In order to compare the properties of the chloride of a γ-ketosulphonic acid with that of ethanedisulphonic acid, which forms an unsaturated compound when boiled with water, an attempt was made to transform the sodium salt into the sulphone chloride. The reaction with phosphorus pentachloride is so vigorous that the principal product is β-chlorpropiophenone—formed by elimination of the sulphonic acid group. The dry sodium salt was, therefore, suspended in phosphorus oxychloride, the mixture cooled in ice water and treated with the calculated quantity of the pentachloride, added in small amounts. The oxychloride was then removed by distillation under diminished pressure. The residue solidified completely. It undoubtedly contained the sulphone chloride. But when it was poured into ice water and the resulting solid dried and recrystallized from chloroform, the crystals that separated were pure acid.

Analysis:

0.1628 gram substance gave 0.3048 gram CO_2 and 0.0732 gram H_2O.

	Calculated for $C_8H_{10}O_4S$.	Found.
C	50.5	51.0
H	4.7	5.0

The acid is readily soluble in water and alcohol, moderately in chloroform, insoluble in ether. It separates from chloroform in colorless needles, melting at 95°. From cold, concentrated water solutions it separates with water of crystallization, but the anhydrous acid is left when water solutions

are evaporated on a steam bath. When the acid is heated under diminished pressure it loses water and sulphur dioxide above 120°. A small quantity of vinylphenyl ketone is formed, but the principal product is the brown, nonvolatile residue that always results from superheating the unsaturated ketone.

Reaction with Organic Magnesium Compounds.—The unsaturated ketone was allowed to react with methylmagnesium iodide and phenylmagnesium bromide in ethereal solution. The products were isolated as described in earlier papers. In each case a test for unsaturated compounds was made by treating a part of the product with a solution of potassium permanganate in acetone, and in each case the result was negative. The only substance obtained with methylmagnesium iodide was normal propylphenyl ketone, which was identified by its boiling point—225°—and by the melting point of the semicarbazone—188°. Phenylmagnesium bromide gave only β-phenylpropiophenone, identified by its melting point, 72°, and by comparison with a specimen on hand. The reaction between vinylphenyl ketone and organic magnesium compounds, therefore, consists exclusively in 1,4-addition:

$$CH_2 : CHCOC_6H_5 + RMgBr = RCH_2CH : C(OMgBr)C_6H_5.$$

α,β-Dibromethyl-4-bromphenyl Ketone, $CH_2BrCHBrCOC_6H_4Br$.—This ketone was used in the hope of getting a solid unsaturated ketone. It was made from dibrompropionyl chloride and brombenzene by the Friedel and Crafts reaction. The procedure was exactly the same as that used for making dibrompropiophenone and the yield was equally good. The ketone is much more soluble in organic solvents than dibrompropiophenone. It separates from alcohol and from ligroin in large prisms or tables, melting at 74°.

Analysis:

0.2122 gram substance gave 0.2272 gram CO_2 and 0.0401 gram H_2O.

	Calculated for $C_9H_7OBr_3$.	Found.
C	29.1	29.2
H	1.9	2.1

β-Ethoxyethyl-4-bromphenyl Ketone, $C_2H_5OCH_2CH_2COC_6H_4Br$.—The reaction between the brom-ketone and potassium iodide was carried out as in the case of dibrompropiophenone. The colorless oil that separated when the product was poured into a solution of sodium thiosulphate partially solidified on standing. The solid was separated and recrystallized from alcohol, from which it separated in large colorless plates, melting at 54°.

Analysis:

0.1940 gram substance gave 0.3669 gram CO_2 and 0.0883 gram H_2O.

	Calculated for $C_{11}H_{13}O_2Br$.	Found.
C	51.4	51.6
H	5.1	5.2

The substance is readily soluble in all common organic solvents except low-boiling ligroin.

The *phenylhydrazone,* $C_2H_5OCH_2CH_2C(C_6H_5) : NNHC_6H_5$, crystallizes from alcohol in pale yellow plates, melting at 108°. It is readily soluble in ether, moderately in alcohol.

Analysis:

0.2004 gram substance gave 0.4321 gram CO_2 and 0.1028 gram H_2O.

	Calculated for $C_{17}H_{19}ON_2Br$.	Found.
C	58.8	58.8
H	5.5	5.7

The oil formed along with ethoxyethylbromphenyl ketone in the reaction with potassium iodide was tested with bromine and found to consist mainly of unsaturated ketone. An attempt to distil it under diminished pressure, after it had been dried in ethereal solution, resulted in complete decomposition. In a second experiment the oil was freed as far as possible from ethoxy compound before distillation. For this purpose a part of it was dissolved in low-boiling ligroin and the solution cooled in a freezing mixture in contact with some of the solid ethoxy compound. The test with bromine showed that 91 per cent. of the liquid left after removing the solid and evaporating the ligroin was vinylbromphenyl ketone, but

this product also decomposed below the boiling point under 18 mm. pressure. The remainder of the liquid was distilled with steam. The first distillates were rich in unsaturated ketone, but likewise decomposed before distillation.

III. Propenylphenyl Ketone.

Dibrombutyryl Chloride, $CH_3CHBrCHBrCOCl$.—The starting point in the preparation of propenylphenyl ketone was the solid crotonic acid. This was treated with bromine and the resulting dibrombutyric acid transformed into the chloride without previous purification. The yield of the latter was excellent—298 grams of pure chloride from 100 grams of crotonic acid. The chloride is a colorless liquid boiling at 112° (20 mm.).

Analysis:

I. 0.1231 gram substance gave 0.2446 gram silver halide.

II. 0.1120 gram substance gave 0.2224 gram silver halide.

	Calculated for $C_4H_5OBr_2Cl$.	Found. I.	II.
BrCl	74.9	75.3	75.0

Dibrombutyrophenone, $CH_3CHBrCHBrCOC_6H_5$.—The bromketone was made and purified like dibrompropiophenone. It crystallizes in needles and melts at 112°.

Analysis:

0.1615 gram substance gave 0.2311 gram CO_2 and 0.0480 gram H_2O.

	Calculated for $C_{10}H_{10}OBr_2$.	Found.
C	39.2	39.0
H	3.3	3.3

Propenylphenyl Ketone, $CH_3CH : CHCOC_6H_5$.—The reaction between the bromketone and potassium iodide was carried out as in previous cases, but as the ethereal solution of the unsaturated ketone extracts a compound containing sulphur and iodine from the solution in which iodine is removed with thiosulphate, it was found to be better to adopt a different method of isolating the unsaturated ketone. The alcoholic solution was poured into an excess of thiosulphate and the ketone extracted with ether as in previous cases. The ether was re-

moved and the residue distilled with steam before the distillation under diminished pressure. The ketone was then separated from the aqueous distillates, dried in ethereal solution with calcium chloride and distilled under diminished pressure. A single distillation gave a colorless liquid boiling constantly at 135° (20 mm.). The test with bromine showed that this was pure propenylphenyl ketone. The yield was 90 per cent. of the calculated amount.

Analysis:

0.1242 gram substance gave 0.3730 gram CO_2 and 0.0775 gram H_2O.

	Calculated for $C_{10}H_{10}O$.	Found.
C	82.2	81.9
H	6.8	6.9

1,3,5-Diphenylmethylpyrazoline, $C_6H_5N(N{=}CC_6H_5)CH_2CHCH_3$.—Five grams of phenylhydrazine were added to an equal weight of ketone dissolved in 25 cc. of alcohol to which a few drops of glacial acetic acid had been added. As there was no evidence of action at the ordinary temperature the mixture was boiled for several hours. The pyrazoline separated in thin yellow plates when the liquid was allowed to cool. It was washed with alcohol and recrystallized from absolute alcohol. It melts at 108°, is sparingly soluble in alcohol and acetone, readily in ether. The solutions in alcohol show a green fluorescence.

Analysis:

0.1211 gram substance gave 0.3615 gram CO_2 and 0.0770 gram H_2O.

	Calculated for $C_{16}H_{16}N_2$.	Found.
C	81.3	81.4
H	6.8	7.1

Reaction with Organic Magnesium Compounds.—The ketone was allowed to react with methylmagnesium iodide and phenylmagnesium bromide. The products were isolated in the usual way and tested for unsaturated compounds with potassium

permanganate dissolved in acetone. No unsaturated compound was formed in either case. The only substance formed when methylmagnesium iodide was used was isovalerophenone, recognized by its boiling point—226°—and the melting point of its oxime. Similarly, phenylmagnesium bromide gave only β-phenylbutyrophenone, identified by comparison with a specimen on hand. The reaction between propenylphenyl ketone and organic magnesium compounds, therefore, consists exclusively of 1,4-addition to the unsaturated ketone:

$$CH_3CH : CHCOC_6H_5 + RMgBr = CH_3CH(R)CH : C(OMgBr)C_6H_5.$$

Crotonyl Chloride, $CH_3CH : CHCOCl$.—In view of the great difference in activity of vinylphenyl ketone and propenylphenyl ketone it seemed worth while to undertake the preparation of the latter by the Friedel and Crafts reaction. To this end crotonic acid was neutralized with sodium carbonate, and the sodium salt dried to constant weight at 135° and treated with phosphorus oxychloride as described in the preparation of the chloride of acrylic acid. The yield of chloride was good, 90 grams of pure product from 100 grams of sodium salt. The chloride is a colorless liquid boiling at 126°.

Analysis:

I. 0.1311 gram substance gave 0.1820 gram AgCl.
II. 0.1180 gram substance gave 0.1638 gram AgCl.

	Calculated for C_4H_5OCl.	Found. I.	Found. II.
Cl	34.0	34.3	34.3

A little more than the calculated amount of finely ground aluminium chloride was added gradually to a solution of 50 grams of crotonyl chloride and 50 grams of benzene in 150 cc. of carbon bisulphide that was cooled in a freezing mixture. The aluminium chloride dissolved rapidly without producing any evolution of gas. The vessel containing the solution was therefore placed in ice water and exposed to direct sunlight. This started brisk evolution of hydrogen chloride and deposition of a colorless crystalline aluminium derivative. The reaction was complete after exposure for 15 min-

utes. The product was poured into iced acid, the organic substances extracted with ether, dried, and distilled under diminished pressure after the solvents had been removed. The liquid began to boil at 135° (20 mm.) and most of the product distilled at 135°–140°. The temperature then rose rapidly and a second colorless distillate was collected between 175° and 185°. Less than half a gram of residue was left in the distilling flask.

A test with bromine showed that the first distillate was almost pure propenylphenyl ketone. On redistillation it yielded 44 grams of pure ketone.

The second distillate (175°–185°) solidified on standing. It was recrystallized from methyl alcohol and was thus obtained in large colorless plates, melting at 74°.

Analysis:

0.1306 gram substance gave 0.4098 gram CO_2 and 0.0870 gram H_2O.

	Calculated for $C_{10}H_{10}O$.	Found.
C	85.8	85.5
H	7.2	7.4

The composition indicated a compound formed by addition of benzene to propenylphenyl ketone and by comparison with a specimen on hand the substance was identified as β-phenylbutyrophenone, $C_6H_5CH(CH_3)CH_2COC_6H_5$. As the results of this experiment show, this is a much better method for making the unsaturated ketone.

Propenylbromphenyl Ketone, $CH_3CH : CHCOC_6H_4Br$.—The preceding experiment was repeated, but with the use of brombenzene in place of benzene. The product gave 30 grams of a distillate boiling at 160°–180° (20 mm.) from 40 grams of crotonyl chloride. The colorless liquid solidified in a freezing mixture. The solid was recrystallized from methyl alcohol.

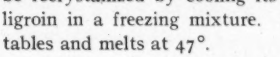
Analysis:

0.1611 gram substance gave 0.3135 gram CO_2 and 0.0535 gram H_2O.

	Calculated for $C_{10}H_9OBr$.	Found.
C	53.3	53.1
H	4.0	4.0

The ketone liquefies in contact with organic solvents but can be recrystallized by cooling its solution in methyl alcohol or ligroin in a freezing mixture. It separates in large, colorless tables and melts at 47°.

1,5,3-Phenylmethylbromphenylpyrazoline,



CC_6H_4Br, the product of the reaction between the unsaturated ketone and phenylhydrazine, crystallizes in yellow plates melting at 136°. Its solutions have a much more pronounced fluorescence than those of the corresponding bromine-free compound.

Analysis:

0.1331 gram substance gave 0.2980 gram CO_2 and 0.0620 gram H_2O.

	Calculated for $C_{16}H_{15}N_2Br$.	Found.
C	60.9	61.0
H	4.8	5.2

α,β-Dibrombutyryl-4-bromphenyl Ketone,

$CH_3CHBrCHBrCOC_6H_4Br$, formed by addition of bromine to the unsaturated ketone, crystallizes from methyl alcohol in needles melting at 76°. It is readily soluble in all common organic solvents except low-boiling ligroin.

Analysis:

0.1802 gram substance gave 0.2040 gram CO_2 and 0.0422 gram H_2O.

	Calculated for $C_{10}H_9OBr_3$.	Found.
C	31.2	30.9
H	2.3	2.6

IV. Isobutenylphenyl Ketone.

Dibromisovaleryl Chloride, $(CH_3)_2CBrCHBrCOCl$. — The starting point in the preparation of isobutenylphenyl ketone was β,β-dimethylacrylic acid, which was made in part from isovaleric acid, in part by the much quicker method of Barbier and Léser.[1] The calculated amount of bromine was added

[1] Bull. Soc. Chim., [3] **33**, 815 (1905).

to the acid dissolved in carbon bisulphide, the solvent removed under diminished pressure, and the residue transformed into chloride as in other similar cases. The chloride is much more sensitive than those previously described. To get a good yield it is necessary to carry out the reaction at the lowest possible temperature and to avoid the least excess of phosphorus pentachloride. Under these conditions the yield is satisfactory: 228 grams of chloride of the dibrom acid from 100 grams of the unsaturated acid. The chloride is a colorless liquid boiling at 126°–130° (20 mm.).

Analysis:

0.1210 gram substance gave 0.2275 gram silver halide.

	Calculated for $C_5H_7OClBr_2$.	Found.
BrCl	70.6	70.6

Dibromisovalerophenone, $(CH_3)_2CBrCHBrCOC_6H_5$.—Considerable care is necessary in the preparation of this substance by the Friedel and Crafts reaction. The aluminium chloride derivative of the ketone is much more readily soluble in carbon bisulphide than those previously described, hence the reaction easily leads to secondary products formed by elimination of hydrogen bromide. By keeping the temperature as low as possible and decomposing the aluminium compounds as soon as the first rapid evolution of hydrogen chloride stops, it is possible to get a fairly good yield. The ketone was recrystallized from methyl alcohol. It separated in needles melting at 81°. The yield was 206 grams of pure ketone from 200 grams of chloride.

Analysis:

0.1552 gram substance gave 0.2330 gram CO_2 and 0.0570 gram H_2O.

	Calculated for $C_{11}H_{12}OBr_2$.	Found.
C	41.2	40.9
H	3.8	4.0

Isobutenylphenyl Ketone, $(CH_3)_2C:CHCOC_6H_5$.—The reaction between the bromketone and potassium iodide was carried out like that with other bromketones and the product

isolated as described under propenylphenyl ketone. The yield of unsaturated ketone was much smaller than that of propenylphenyl ketone—only 60 per cent. of the possible amount.

Analysis:

0.1405 gram substance gave 0.4250 gram CO_2 and 0.0978 gram H_2O.

	Calculated for $C_{11}H_{12}O$.	Found.
C	82.5	82.5
H	7.5	7.7

Isobutenylphenyl ketone is a colorless liquid that boils at 148° (22 mm.). While far less reactive than any other of the unsaturated ketones described in this paper, it is, nevertheless, considerably more reactive than β-phenylbenzalacetophenone, which differs from it only in having 2 phenyl in place of 2 methyl groups. Thus it immediately reduces a cold solution of potassium permanganate in acetone and combines with bromine at the temperature of a freezing mixture—two reactions that do not take place at all with the corresponding phenyl compound.

The *phenylhydrazone* of the ketone was made in the usual way. It crystallizes in almost colorless plates melting at 88°. It is extremely unstable, turning brown and liquefying in the course of a few hours when exposed to light and air, and in a few days when sealed up and kept in the dark.

Analysis:

0.1165 gram substance gave 0.3494 gram CO_2 and 0.0754 gram H_2O.

	Calculated for $C_{17}H_{18}N_2$.	Found.
C	81.6	81.8
H	7.2	7.2

Reaction with Phenylmagnesium Bromide.—The reaction was carried out in the usual way. A test with permanganate showed the presence of unsaturated compounds in the product. It was, therefore, distilled with steam until free from brombenzene and diphenyl, dissolved in ether, dried and frac-

tionated under diminished pressure. It first yielded a small quantity of distillate boiling between 165° and 170°, then the temperature rose rapidly to 185°–187°, where the remainder distilled without leaving a residue. The high-boiling fraction was β-phenylisobutyrophenone.

Analysis:

0.1254 gram substance gave 0.3922 gram CO_2 and 0.0869 gram H_2O.

	Calculated for $C_{17}H_{18}O$.	Found.
C	85.7	85.3
H	7.6	7.7

The *phenylhydrazone* of the ketone crystallizes in large yellow needles melting at 94°.

Analysis:

0.1212 gram substance gave 0.3732 gram CO_2 and 0.0796 gram H_2O.

	Calculated for $C_{23}H_{24}N_2$.	Found.
C	84.0	84.1
H	7.3	7.3

Oximes.—When boiled with hydroxylamine hydrochloride and excess of potassium hydroxide in alcoholic solution, phenylisobutyrophenone formed two oximes that were separated by crystallization from a mixture of ether and ligroin. One crystallizes in needles melting at 85°, the other in plates melting at 111°. Both are readily soluble in alcohol and ether, sparingly in ligroin.

Analysis:

I. 0.1354 gram substance (85°) gave 0.3986 gram CO_2 and 0.0914 gram H_2O.

II. 0.1489 gram substance (111°) gave 0.4373 gram CO_2 and 0.1015 gram H_2O.

	Calculated for $C_{17}H_{19}ON$.	Found. I.	Found. II.
C	80.6	80.3	80.2
H	7.5	7.5	7.6

The low-boiling fraction obtained from the product of the reaction between phenylmagnesium bromide and isobutenyl-

phenyl ketone proved to be a mixture. As it was too small in amount for successful separation it was dissolved in acetone and oxidized with permanganate. The acetone was then removed completely by heating under diminished pressure and the residue distilled with steam. This gave 0.8 gram of benzophenone, proving that the unsaturated compound was due to 1,2-addition to carbonyl. Isobutenylphenyl ketone, therefore, gives two reactions with phenylmagnesium bromide:

I. $(CH_3)_2C : CHCOC_6H_5 + C_6H_5MgBr = (CH_3)_2C(C_6H_5)CH : C(OMgBr)C_6H_5$;

II. $(CH_3)_2C : CHCOC_6H_5 + C_6H_5MgBr = (CH_3)_2C : CHC(OMgBr)(C_6H_5)_2$.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
July, 1909.

[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

ON THE ACTION OF FEHLING'S SOLUTION ON GALACTOSE.

BY ERNEST ANDERSON.

The following pages give a detailed account of a quant tative investigation carried out by myself, at the suggestion and under the direction of Dr. Nef, of the products formed in the oxidation of *d*-galactose by alkaline solutions containing cupric hydroxide (Fehling's solution).

It was found here, as in the case of *d*-glucose, *d*-mannose and *d*-fructose by Nef,[1] that the reaction products are, besides isomeric hexonic acids, carbonic, formic, oxalic, glycollic *d*- and *l*-glycerinic, *l*-threonic, and *d*-erythronic acids. Whereas the members of the *d*-glucose series give much *d*-gluconic and smaller amounts of *d*-mannonic acid, and also probably some α-oxymethyl-*d*-arabonic acid, which was overlooked by Nef[2] in his work, *d*-galactose was found to give much *d*-galactonic and relatively smaller amounts of *d*-talonic acid on treatment with the reagent named; it is highly probable

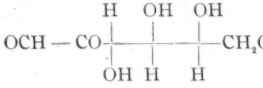
[1] Ann. Chem. (Liebig), **357**, 259–286.
[2] Cf. Ann. Chem. (Liebig), **357**, 298, and thesis of Spoehr, soon to be published.

also that in addition small amounts of α-oxymethyl-*d*-lyxonic acid are formed, but I was unable to prove this by experiment. It is evident also, from my work, that only two of the four possible trioxybutyric acids are formed on treatment of the above named hexoses with alkaline cupric hydroxide—namely, *l*-threonic and *d*-erythronic acids. Furthermore, Dr. Nef tells me he is now convinced, because of my work, that he overestimated the amount of trioxybutyric acids and underestimated the amount of *d*- and *l*-glycerinic acids formed when the ordinary hexoses are treated with Fehling's solution, owing to the difficulty of effecting a sharp separation of these acids.

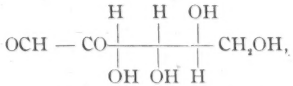
To summarize: The following acids are the reaction products formed by treating *d*-galactose, $OCH(CHOH)_4CH_2OH$, with Fehling's solution: Carbonic; formic; oxalic glycollic, $COOH.CH_2OH$; *d*- and *l*-glycerinic, $COOH.CHOH.CH_2OH$; *l*-threonic, $COOH(CHOH)_2CH_2OH$; *d*-erythronic, $COOH(CHOH)_2CH_2OH$; *d*-galactonic, $COOH(CHOH)_4CH_2OH$; *d*-talonic, $COOH(CHOH)_4CH_2OH$; and α-oxymethyl-*d*-lyxonic, $COOH(CH_2OH)(CHOH)_2CH_2OH$.

In view of all these facts and also especially because of his work on the action of soluble alkaline hydroxides on all possible sugars containing from one to six carbon atoms, which will be published in detail in *Liebig's Annalen*, in 1910, Dr. Nef now considers the following interpretation of the action of Fehling's solution on the ordinary hexoses as the final one; it is really based entirely on the ideas presented in his former paper published in 1907.[1]

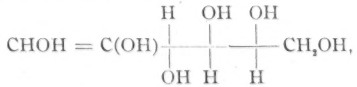
The members of the *d*-glucose and *d*-galactose series give, by oxidation of the alcohol group adjacent to the carbonyl group, the corresponding hexosones,



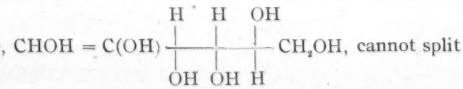
and



which then give, by the benzilic acid rearrangement, the two corresponding hexonic acids. The 1,2-dienol common to mannose, glucose, and levulose,



as well as the 1,2-dienol common to *d*-talose, *d*-galactose, and



d-tagatose, cannot split to any appreciable extent into oxymethylene and the pentose, *d*-arabinose or *d*-lyxose, respectively, since it has not been possible in any case up to the present time to show that any pentonic acid is formed by the action of Fehling's solution on hexoses. The formation of 2,3-dienols, as well as of 3,4-dienols, from the hexoses and their subsequent splitting is a necessary prelude to the formation of the

[1] See especially Ann. Chem. (Liebig), **357**, 294–312.

monobasic acids containing from one to four carbon atoms, as well as of the new hexonic acids, α-oxymethyl-*d*-arabonic and α-oxymethyl-*d*-lyxonic acids, mentioned above.

The 2,3-dienol which is common to *d*-fructose and *d*-pseudo-fructose (2-ketohexoses), and also to α- and β-*d*-glutose (3-ketohexoses), $CH_2OH-COH=COH-\underset{H}{\overset{OH}{CH}}-\underset{H}{\overset{OH}{CH}}-CH_2OH$, as well as the 2,3-dienol common to *d*-tagatose and *l*-sorbose (2-ketohexoses), and to α- and β-*d*-galtose (3-ketohexoses),

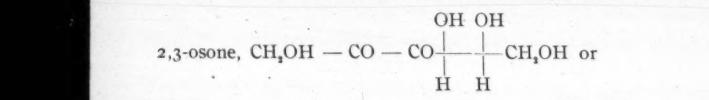
$$CH_2OH-COH=COH-\underset{OH}{\overset{H}{CH}}-\underset{H}{\overset{OH}{CH}}-CH_2OH,$$

then simply breaks, by methylene dissociation, in a manner entirely analogous to the double cyanides, KN : C = C : NAg, RN : C = C : NAg, etc.,[1] into diose, CH_2OHCHO, *d*-erythrose, $OCH-\underset{H}{\overset{OH}{CH}}-\underset{H}{\overset{OH}{CH}}-CH_2OH$, or *l*-threose, $OCH-\underset{OH}{\overset{O}{CH}}-\underset{H}{\overset{OH}{CH}}-CH_2OH$, respectively. Diose then gives, by oxidation with Fehling's solution, glyoxal, whereas the two tetroses must give one and the same *d*-tetrosone, $CHO-CO-\underset{H}{\overset{OH}{CH}}-CH_2OH$; these two osones then give, by a benzilic acid rearrangement, glycollic acid, on the one hand, and two trioxybutyric acids, namely, *l*-threonic and *d*-erythronic acids, on the other. Obviously some of the diose thus formed dissociates further, through formation of the dienol, CHOH = CHOH, into two molecules of oxymethylene, =CHOH, which, of course, then gives formic acid by further oxidation.

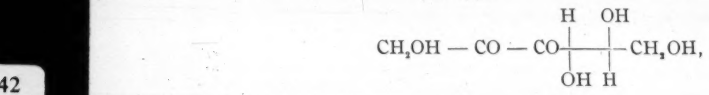
The 3-ketohexoses, α- and β-*d*-glutose and α- and β-*d*-galtose, which are formed by the action of alkalies on the corre-

[1] Nef: Ann. Chem. (Liebig), **298**, 215, 313; and THIS JOURNAL, **30**, 466, footnote.

sponding aldohexoses, give, as has been sharply proved by Spoehr's work, through an intermediate formation of the

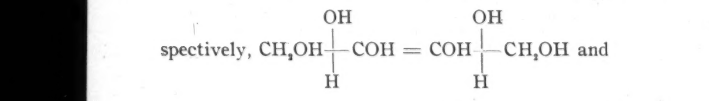


2,3-osone, $CH_2OH - CO - CO - CH(OH) - CH(H) - CH_2OH$ or



$CH_2OH - CO - CO - CH(H) - CH(OH) - CH_2OH$,

and subsequent *entire* asymmetric benzilic acid rearrangement, only α-oxymethyl-*d*-arabonic or α-oxymethyl-*d*-lyxonic acid, respectively. The 3-ketohexoses finally are the intermediate products which are the source of all the *d*- and *l*-glycerinic acid formed by the action of Fehling's solution on all aldohexoses. The 3,4-dienols which are common to α-*d*-glutose and α-*d*-galtose and to β-*d*-glutose and β-*d*-galtose, re-



spectively, $CH_2OH - CH(OH) - COH = COH - CH(OH) - CH_2OH$ and

$CH_2OH - CH(OH) - COH = COH - CH(H) - CH_2OH$,

must in all cases, as soon as formed, spontaneously dissociate into two molecules of *d*- or *l*-glyceric aldehyde; these products then give, by oxidation, mainly glycerosone,

$$CH_2OHCO—CHO,$$

which, by a benzilic acid rearrangement, gives equal amounts of *d*- and *l*-glycerinic acid. The members of the *d*-glucose series give relatively far more glycerinic acid than those of the *d*-galactose series for exactly the same reason that the *d*-glucose series gives relatively more *d,l*-lactic acid, as compared with the *d*-galactose series, when treated with caustic alkalies—namely, because there is more formation of 3,4-dienol, and

consequent spontaneous dissociation into two molecules of triose, in the former than in the latter case.[1]

Finally, the formation of small amounts of carbonic and oxalic acids from hexoses by the action of alkaline cupric hydroxide is best explained on the assumption that the various osones oxidize partially to α-keto acids,[2] which then lose carbon dioxide, giving a lower homologous sugar and in part, also, through enol formation and subsequent dissociation, give glyoxylic acid, etc.; thus tetrosone, for example, could give, by oxidation of the aldehyde group, the α-keto acid,

$$CH_2OH—CHOH—CO—COOH,$$

which, as dienol,

$$CH_2OHCOH = COH—COOH,$$

must automatically dissociate into diose and glyoxylic acid.[3]

EXPERIMENTAL PART.

A solution of 382.5 grams copper vitriol in two liters of water was mixed in the cold, as directed by Nef,[4] with a solution of 183.9[5] grams of sodium hydroxide in 688 cc. of water, *i. e.*, with 61.3 grams more sodium hydroxide than the amount necessary for the formation of cupric hydroxide. Then a solution of 59 grams of *d*-galactose melting at 152°–154°, the exact amount necessary as determined by previous tests, in 250 cc. water was added. The mixture was placed at once in a large

[1] Nef: Ann. Chem. (Liebig), **357**, 300.

[2] Cf. Nef: *Ibid.*, **357**, 258.

[3] An entirely analogous interpretation holds for the products formed by the action of Fehling's solution on aldopentoses; since my experiments (soon to be published) prove that the tetroses, through intermediate formation of 2,3-dienols, dissociate mainly into two molecules of diose, it follows that the large amount of glycollic acid observed by Mr. Anderson in his work on *d*-galactose comes mainly through a splitting of this sugar, in two steps, into three molecules of glycollic aldehyde. Finally, I would like to emphasize here that all sugars containing from two to six carbon atoms in the molecule, when treated in alkaline solution with air, give exactly the same products and in relatively the same amounts as when cupric hydroxide is present (*i. e.*, as with Fehling's solution). It is therefore my intention not to repeat the work with Fehling's solution, but to determine with students, by sharper quantitative methods, the nature of all the products formed by treating various sugars in alkaline solution with a rapid stream of air.—J. U. Nef.

[4] Ann. Chem. (Liebig), **357**, 217.

[5] The weight given is corrected to 100 per cent. sodium hydroxide. I used 191.2 grams sodium hydroxide, 96.2 per cent. pure.

bath of boiling water and heated for two hours, with frequent shaking. Cuprous oxide appeared two minutes after mixing the solutions, when the inside temperature was only 30°. The reaction was complete in twelve minutes, when a temperature of 60° had been reached. As soon as the cuprous oxide had settled, the clear, slightly yellow solution was filtered hot; the cuprous oxide was washed by decantation four times and finally on the filter with hot water. These operations were repeated with a second portion of 59 grams *d*-galactose and the combined aqueous filtrates were then worked up for nonvolatile acids. The amount of carbon dioxide and of formic acid formed in the oxidation was determined in special experiments as given below.

Determination of Carbon Dioxide.—An aqueous filtrate, obtained as described above, from 58 grams of *d*-galactose, etc., was diluted to five liters with water and the amount of carbon dioxide in one liter was then determined quantitatively as directed by Nef.[1] This gave 1.51 grams of barium carbonate from one liter, or a total of 7.55 grams of barium carbonate from the five liters. In a special determination, 25 grams of the sodium hydroxide used gave 0.28 gram of barium carbonate; 187.6 grams of sodium hydroxide, *i. e.*, the amount used with the 58 grams *d*-galactose, would therefore give 2.10 grams of barium carbonate. Correcting for this amount of barium carbonate, 58 grams of the sugar gave 1.22 grams carbon dioxide; hence 100 grams *d*-galactose give 2.11 grams of carbon dioxide.

Determination of Formic Acid.—In order to set free the volatile, as well as the nonvolatile acids, an aqueous filtrate obtained from 58 grams *d*-galactose, as directed above, was treated with exactly the calculated amount of hydrogen chloride, *i. e.*, with the amount necessary to neutralize one-third of the total amount of sodium hydroxide originally used; water and formic acid were then distilled off under 15–30 mm. pressure, finally on the boiling water bath. The distillate was diluted to four liters with water and the formic acid determined by titration with 0.1 N potassium hydrox-

[1] Ann. Chem. (Liebig), **357**, 219.

ide, phenolphthalein being used as the indicator; 250 cc. of the distillate required 107.8 cc. of 0.0974 N potassium hydroxide. The total amount of formic acid given by 58 g ams *d*-galactose is therefore 7.73 grams and by 100 grams *d*-galactose is 13.3 grams.

Separation of the Nonvolatile Acids.—The nonvolatile acids left with the salt residue after treating the aqueous filtrates obtained from two portions of 59 grams *d*-galactose with the calculated amount of hydrogen chloride and removing the volatile acids as stated above, were now worked up as follows. Extraction with two liters of hot 95 per cent. alcohol gave a total of 121 grams gum, which was freed from inorganic salts and resolved into three fractions. First it was digested with four liters of ethyl acetate, which took up 87.5 grams gum. The insoluble portion left, on digesting with 1500 cc. absolute alcohol, 18.9 grams inorganic salts, and the filtrate gave, on removal of the solvent in the usual manner (at 100° and 15–30 mm.), 14.6 grams least soluble gum C. The 87.5 grams gum soluble in acetic ether was now resolved, by dissolving in 50 cc. absolute alcohol and subsequent addition of 500 cc. ether, into 33.8 grams soluble gum A, and 53.7 grams of precipitated gum B. Fraction A contains the glycollic acid mainly; fraction B consists of glycerinic and trioxybutyric acids mainly, but contains also some hexonic acids; while fraction C is mainly a mixture of *d*-galactonic and talonic acids; there also appear in the course of the various subsequent operations, especially on treating fractions B and C with quinine, varying amounts of a gum which is difficultly soluble in spirit and practically insoluble in absolute alcohol and which seems to be analogous to Nef's so-called polygluconic acid;[1] the nature of this neutral product, which I call polygalactonic lactone, could not be determined, but it is certainly not a primary reaction product and its formation could at times be entirely avoided.

There are two methods by which the components of fractions A, B and C can be separated: *d*-talonic and *d*-galactonic acids may in great part be removed from fractions B and C by direct treatment in the cold with equal volumes of alcohol and phenyl-

[1] Ann. Chem. (Liebig), **357**, 268, 276, 281.

hydrazine.[1] Since, however, these two acids give low-melting (110°–130°) brucine salts which can be partly, but not sharply, separated, by crystallization from alcohol, from the high-melting brucine salts formed by *d*- and *l*-glycerinic, as well as by all the four isomeric trioxybutyric acids, I preferred to accomplish first a partial separation of the various acids by fractional crystallization of the brucine salts into low- (90°–110°) and high- (190°–210°) melting salts and then to treat only the acids giving low-melting brucine salts with phenylhydrazine; the *d*-galactonic and *d*-talonic acid phenylhydrazides, which separate out, could then be sharply separated by boiling out with much absolute alcohol in which the former is practically insoluble.

The separation of the monobasic acids containing three and four carbon atoms in the molecule, all giving high-melting (205°–220°) brucine salts which are difficultly soluble in absolute alcohol, was found exceedingly difficult: *d,l*-glycerinic brucine, as has been shown by Neuberg,[2] can be separated into its components by crystallization from alcohol (*but not sharply, as I have found*) since *d*-glycerinic brucine, $[\alpha]_D^{20} = -33°.2$, is far less soluble. Preliminary unpublished experiments by Nef, which I have confirmed, show that *d,l*-glycerinic quinine can be very completely separated into its optical components, since *l*-glycerinic quinine is very difficultly soluble in cold water, whereas *d*-glycerinic quinine is very soluble.

Nevertheless, I finally succeeded in proving very sharply that the acids giving high-melting brucine salts consisted mainly of equal amounts of *d*- and *l*-glycerinic acid, and that only a small amount of *l*-threonic and still less *d*-erythronic acid was present. The *l*-threonic acid separated out in great part as a difficultly soluble phenylhydrazide on treatment of the gum obtained from the least soluble high-melting brucine salts with phenylhydrazine and alcohol. The presence of very small amounts of *d*-erythronic acid, on the other hand, could be established only by oxidation to mesotartaric acid.

[1] Cf. Nef: Ann. Chem. (Liebig), **357**, 261.
[2] Ber. d. chem. Ges., **37**, 340.

Glycollic Acid, Gum A.—On digesting gum A, 33.8 grams, on the boiling water bath for 9 hours with water and an excess of pulverized strychnine, 106 grams of the alkaloid dissolved. The strychnine salts, after distilling off the water under 15–30 mm. pressure, gave, on dissolving in alcohol and letting stand, a total of 69.9 grams of crude glycollic strychnine, melting from 160° to 200°; from this, on digestion for 10 hours on a boiling water bath with water and an excess of powdered quicklime, subsequent filtration, concentration, etc., 20.1 grams of crystalline calcium glycollate were finally obtained, corresponding to 11.75 grams anhydrous glycollic acid.

0.9608 gram air-dried salt lost, on drying at 100°–120°, 0.2716 gram H_2O.

0.6892 gram anhydrous salt, on ignition, gave 0.2016 gram CaO.

	Calculated for $Ca(C_2H_3O_2)_2 4H_2O$.	Found.
H_2O	27.48	28.23
CaO	29.47	29.25

The 69.9 grams gummy strychnine salts which were left in the alcoholic filtrates gave back, on treating with an excess of aqueous sodium hydroxide, filtering off the alkaloid, adding the calculated amount of hydrochloric acid, removing the water by distillation under a pressure of 15–30 mm. and, finally, extracting the salt residue with acetic ether, a total of 18.6 grams of acid gum, mainly glycerinic and trioxybutyric acids, all of which give high-melting (200°–220°) brucine salts, which crystallize beautifully from absolute alcohol. The gum was therefore diluted with water to 500 cc.; 10 cc. of this solution, corresponding to 0.372 gram gum, required 33.22 cc. 0.1 N potassium hydroxide for neutralization, *i. e.*, by heating for ten minutes on the boiling water bath with a decided excess of 0.1 N potassium hydroxide, the excess of alkali being then titrated with 0.1 N hydrochloric acid and phenolphthalein as indicator.[1] The main

[1] This method has subsequently been found to give too high (about 10 per cent.) results, so that some free brucine was invariably present on treating the main portion of my acid gums with the calculated amount of alkaloid.

portion of the acid gum in water was now converted into brucine salts in the usual way, *i. e.*, by adding a small volume of alcohol and the amount of brucine calculated[1] on the basis of the titration, 64.13 grams, digesting on the boiling water bath for one hour after complete solution of the alkaloid and then distilling off the water under a pressure of 15–30 mm., heating finally to 80°. On dissolving the salts thus obtained in an equal weight of absolute alcohol a total of 37.5 grams, in four portions, of crystalline high-melting (208°–210°) salts were obtained. The gummy brucine salts, weighing 42 grams and containing some free brucine, gave back, on treating in aqueous solution with sodium hydroxide, filtering off the brucine, extracting the alkaline solution with chloroform, adding the calculated amount of hydrochloric acid, and finally distilling off the water under 15–30 mm. pressure and extracting the salt residue with absolute alcohol, a total of 8.5 grams acid gum, which was united with 10.2 grams of analogous gum obtained from fraction B.

Fraction B, 53.7 Grams.—Gum B was diluted with water to one liter; 10 cc. of this solution, containing 0.537 gram, required 43.28 cc. 0.1 N potassium hydroxide for neutralization.[1] The main portion of the solution, on treatment with the calculated amount, 168.9 grams, brucine gave 255 grams crude brucine salts still containing some water. These were separated by crystallization from alcohol into four fractions: 57.7 grams salts melting from 90° to 110°; 61.3 grams melting from 90°–100°; 33.2 grams melting from 206°–208; and finally 60 grams gummy salts. The nature of the first three crystalline fractions will be discussed in detail later. The 60 grams noncrystalline salts gave, on conversion to the free acids in the usual way, 10.2 grams acid gum, soluble in absolute alcohol, which was united with 8.5 grams of gum recovered from fraction A. This was now resolved, by dissolving in 20 cc. absolute alcohol and adding 350 cc. of ether, into 11 grams of soluble gum and 7 grams of precipitated gum; the latter was united with 9 grams of difficultly soluble gum obtained from fraction C (see below). The 11 grams of

[1] See footnote, p. 410.

soluble gum, on the other hand, yielded no more strychnine glycollate on conversion into strychnine salts, and gave back 10.1 grams of gum soluble in absolute alcohol, and this, after titration of 0.2 gram, which required[1] 19 cc. 0.1 N potassium hydroxide, was converted in the usual manner into brucine salts. Crystallization of these from alcohol gave a total of 27.1 grams, in three crops, of crystalline salts melting from 90° to 110°, besides 20 grams noncrystalline salts which were united with a corresponding fraction from gum D (see below).

Fraction C, 14.6 Grams.—Gum C was diluted with water to 250 cc.; 5 cc. of this solution, containing 0.292 gram of gum, required 22.2 cc. 0.1 N potassium hydroxide for neutralization.[2] The main portion gave, on treatment with 42.86 grams of brucine, 64 grams crude brucine salts which, on crystallization from alcohol, gave only 11.1 grams of crystalline salts melting from 90° to 110°. The remainder, about 50 grams gummy salt, gave back with sodium hydroxide, etc., 9 grams of gum soluble in 95 per cent. alcohol, but not entirely in absolute alcohol, and containing, therefore, some polygalactonic lactone; this was now united with a corresponding 7 grams gum from fraction B (see above). The combined gums gave, on heating for 9 hours from 80° to 100° with 48 cc. acetic anhydride,[3] etc., besides 6.5 grams of insoluble gum, tar, and sodium chloride, 16.2 grams acylated gum, soluble in hot ether, which, on fourfold hydrolysis with three parts of water, gave back 10.6 grams gum. This, on dissolving in 20 cc. absolute alcohol and adding 40 cc. ether, was separated into 6.75 grams soluble gum (D), and 3.7 grams precipitated gum (E); the former, after titration of 0.27 gram, which required 24.22 cc. 0.1 N potassium hydroxide, was treated with the calculated[4] amount, 22.9 grams, of brucine. On dissolving the salts in alcohol a total of 10.4 grams high-melting (190°–204°) crystalline brucine salts were obtained.

[1] See footnote, p. 410.
[2] *Ibid.*, p. 410.
[3] Cf. Nef: Ann. Chem. (Liebig), **357**, 239–40.
[4] See footnote, p. 410.

Since experience with *d,l*-glycerinic brucine has shown that this salt is partially resolved by crystallization from alcohol into its optical components, the *d* modification, $[\alpha]_D^{20} = -33°.2$, being far less soluble in alcohol whereas the *l* modification, $[\alpha]_D^{20} = -22°$, is decidedly more soluble and often comes out very slowly from alcohol, it was thought probable that the various gummy brucine salts mentioned above might still contain appreciable quantities of *l*-glycerinic brucine; this could easily be ascertained by conversion of the acids into the quinine salts in which the presence of *l*-glycerinic quinine melting at 184°, which is very difficultly soluble in cold water, could then easily be recognized. The alcoholic mother liquors from the 10.4 grams high-melting brucine salts mentioned above were therefore united with 20 grams of analogous gummy brucine salts obtained from fraction B, and in all 7.3 grams acid gums were recovered from these by sodium hydroxide, etc. These gums took up 17.3 grams quinine on digestion for 8 hours in aqueous solution on a boiling water bath, but on crystallizing the salts obtained from water, only 6.6 grams of quinine salts, melting from 120° to 130° on repeated crystallization, and therefore probably consisting of impure *l*-glycerinic quinine, were obtained. The aqueous filtrate, still containing about 13.2 grams salts, was found to contain a small amount of neutral polygalactonic lactone, which was removed by dissolving in absolute alcohol; the remainder gave back, with sodium hydroxide, etc., 3 grams of acid gum (F).

On treating gum E, 3.7 grams, after titration of 0.296 gram, which required 18.3 cc. 0.1 N potassium hydroxide, with the calculated amount, 8.3 grams, of brucine, no crystalline salts were obtained and the recovered acid gums, 3.5 grams, gave, on treatment with 3.5 cc. each of alcohol and phenylhydrazine, after standing 24 hours in the cold, 0.4 gram *d*-galactonic phenylhydrazide, melting from 195° to 200°. The gummy hydroxides, soluble in alcohol, on being hydrolyzed as directed by Nef,[1] gave back 2.8 grams of acid gum; this, on long digestion in aqueous solution with quinine, took up

[1] Ann. Chem. (Liebig), **357**, 228.

5.1 grams of alkaloid. On crystallization of the salts obtained from water, only 0.2 gram of a crystalline salt, melting at 160°, which was probably *l*-glycerinic quinine, was obtained. The filtrate was found to contain some polygalactonic lactone and finally gave back, with sodium hydroxide, etc., 1.2 grams of acid gum, which will be referred to later on.

Summary.

The resolution of the 102.1 grams nonvolatile acid gums from 118 grams *d*-galactose, which has been described in some detail on the preceding pages, may be briefly summarized as follows: I. A total of 157.2 grams low-melting (90°–110°) brucine salts were obtained in four fractions of 57.7, 61.3, 27.1 and 11.1 grams; these consist, as will be shown later in this paper, largely of *d*-galactonic and *d*-talonic brucine, but a fair amount of glycerinic and trioxybutyric brucine salts is also present. II. 81.1 grams high-melting (190°–210°) brucine salts of *d*- and *l*-glycerinic, *l*-threonic and *d*-erythronic acids in three fractions of 37.5, 10.4 and 33.2 grams. III. 20.1 grams crystallized calcium glycollate. In addition, 3.0 grams gum (F) and 1.2 grams gum (from E) have not been identified in the form of crystalline derivatives; finally, a fair amount of neutral polygalactonic lactone gum was obtained in the course of the various operations employed, besides 0.4 gram crystallized *d*-galactonic phenylhydrazide and 6.6 grams crude *l*-glycerinic quinine melting from 120° to 130°.

I. d-*Galactonic and* d-*Talonic Acid from the Low-melting Brucine Salts.*—The two acids just named can be separated, as Fischer[1] has shown, by means of the cadmium salts. They can also be separated by means of the hydrazides and I have used the latter method exclusively in my work. Fraction I., 57.7 grams brucine salts obtained from oil B and melting from 90° to 110°, gave, when treated with sodium hydroxide, etc., 17.5 grams of acid gum; this, on treatment with 17.5 cc. alcohol and 17.5 cc. phenylhydrazine gave, after standing 24 hours, 15.7 grams insoluble crystalline hydrazides melting at 185° after being well washed with cold alcohol; the results

[1] Ber. d. chem. Ges., **24**, 3623.

obtained with the alcoholic filtrate are described further on. On crystallizing the insoluble hydrazides from about 30 cc. hot water, 13.1 grams of practically pure *d*-galactonic phenylhydrazide, melting from 200° to 205°, were obtained; the aqueous filtrate distilled off at reduced pressure gave 2.6 grams *d*-talonic phenylhydrazide melting from 150° to 155°. The *d*-galactonic phenylhydrazide finally was recrystallized once more before analysis by dissolving in five parts of hot water, filtering and adding about twenty parts of absolute alcohol; it separates out in colorless leaflets pointed at one end and melting from 203° to 205°.

0.1942 gram, dried *in vacuo*, gave 0.3596 gram CO_2 and 0.1212 gram H_2O.

0.1984 gram, dried *in vacuo*, gave 17.20 cc. N at 18°.5 and 744.6 mm.

	Calculated for $C_{12}H_{18}O_6N_2$.	Found.
C	50.35	50.51
H	6.29	6.99
N	9.79	9.86

An optical determination gave: $d = 1.005$; $p = 2.201$; *i. e.*, 0.5609 gram substance and 24.9228 grams water; $[\alpha]$ in a 1 dcm. tube $= +0°.231$, whence $[\alpha]_D^{20} = +10°.44$.

For comparison, I also made *d*-galactonic acid from *d*-galactose by oxidation with bromine, using in general the method of Kiliani.[1] Three grams of the acid, obtained from the crystallized calcium salt, gave, on treatment with phenylhydrazine and alcohol in the cold, 3.9 grams of crystals melting from 190° to 200°; these, when recrystallized from water and alcohol as mentioned above, gave leaflets, pointed at one end, melting from 203° to 205°. An optical determination gave: $d = 1.005$; $p = 2.051$; *i. e.*, 1.0434 grams of substance and 49.8356 grams of water; $[\alpha]$ in a 2 dcm. tube $= +0°.447$, whence $[\alpha]_D^{20} = +10°.84$.

The 2.6 grams of crude *d*-talonic phenylhydrazide mentioned above was recrystallized from fifty parts of hot absolute alcohol and gave, on cooling, a large amount of crystals melting between 161° and 162°.

[1] Ber. d. chem. Ges., **18**, 1552.

0.1929 gram, dried *in vacuo*, gave 0.3550 gram CO_2 and 0.1146 gram H_2O.

0.2004 gram, dried *in vacuo*, gave 17.32 cc. N at 17° and 734.5 mm.

	Calculated for $C_{12}H_{18}O_6N_2$.	Found.
C	50.35	50.19
H	6.29	6.66
N	9.79	9.77

An optical determination gave: $d = 1.011$; $p = 3.995$; *i. e.*, 0.5600 gram substance and 13.4572 grams of water; $[\alpha]$ in a 1 dcm. tube = —1°.00, whence $[\alpha]_D^{20}$ = —24°.75.

Finally, *d*-galactonic acid, by treatment with pyridine and water, as directed by Fischer,[1] was converted into a mixture of *d*-galactonic and *d*-talonic acids. This mixture, on treatment with phenylhydrazine, etc., gave a large amount of *d*-galactonic hydrazide melting from 190° to 200°, and a smaller amount of crude *d*-talonic hydrazide melting between 150° and 155°. The latter, after two crystallizations from fifty parts hot absolute alcohol, gave a pure product melting between 161° and 162°; the optical investigation gave: $d = 1.011$; $p = 3.6525$; *i. e.*, 0.4462 gram substance and 11.7700 grams water; $[\alpha]$ in a 1 dcm. tube = 0°.92; whence $[\alpha]_D^{20}$ = —24°.91. Fischer gives the melting point 155° for *d*-talonic phenylhydrazide; the product was probably not absolutely pure, since I have observed that when my synthetic *d*-talonic phenylhydrazide melted at 155° it gave $[\alpha]_D^{20}$ = —22°.84 in 4 per cent. concentration, but on further recrystallization the melting point invariably rose to 161°–162° and the specific rotation to the value just given. From the data given it is evident that the product obtained by me from *d*-galactose and Fehling's solution was *d*-talonic phenylhydrazide.

The above mentioned alcoholic filtrate from the 15.7 grams crude mixture of *d*-galactonic and *d*-talonic phenylhydrazides, which contained the alcohol-soluble hydrazides, gave back, after hydrolysis according to the method of Nef,[2] 8.5 grams of acid gum; 0.33 gram of this required 21.5 cc.

[1] Ber. d. chem. Ges., **24**, 3623.

[2] *Loc. cit.*

of 0.1 N potassium hydroxide for neutralization. The remainder was therefore treated with the calculated amount, 20.32 grams, of brucine. The brucine salts gave, on crystallization from 90 per cent. alcohol, 4.4 grams, crop I, melting at 156°, and shown later to be pure *d*-talonic brucine, and 8.26 grams, crop II, melting from 130° to 138°. The latter, on treatment with sodium hydroxide, etc., gave 2 grams of gum which, mixed in the usual manner with phenylhydrazine and alcohol, gave only 0.85 gram crystalline hydrazide melting from 180° to 185°, which was resolved by digestion with hot alcohol into 0.6 gram *d*-galactonic phenylhydrazide melting at 198°–200°, and 0.25 gram crude *d*-talonic phenylhydrazide melting 150°–155°. The alcoholic filtrates containing the soluble gummy hydrazides, including a small amount from fraction II, described below, gave back, on hydrolysis, 2.0 grams of acid gum which was united with the 3.0 grams of gum F, mentioned above, and treated with 10 grams of brucine; the salts obtained gave, on crystallization from alcohol, 2.45 grams crystalline salt melting at 150°, which is shown below to be practically pure *d*-talonic brucine. The alcoholic filtrate gave back 3.4 grams acid gum which gave no further crystalline hydrazides on treatment with phenylhydrazine and alcohol; the gummy hydrazides were therefore united with a corresponding fraction referred to below, which was obtained from 27.1 grams low-melting salts from fraction D.

Fraction II, low-melting brucine salts, 61.3 grams obtained from B as well as 11.1 grams of a corresponding salt from C, gave, on treatment with sodium hydroxide, etc., 18.6 grams of gum; this gave, on treatment with 19 cc. each of alcohol and phenylhydrazine, noticeably less insoluble crystalline hydrazides, 5.7 grams, than was the case with crop I, just described. Furthermore, the mixture was resolved by crystallization from hot water into 5 grams *d*-galactonic hydrazide melting at 200° and 0.7 gram insoluble oxalyl hydrazide melting from 230° to 260°. Oxalyl hydrazide, which was also made for comparison from oxalic acid and phenylhydrazine by mixing in alcoholic solutions, is very difficultly solu-

ble even in boiling water or alcohol; it can be recrystallized from 5 per cent. sodium carbonate solution as directed by Bülow,[1] but is partly decomposed by the operation. On digesting the 0.7 gram mentioned above with 800 cc. hot alcohol only a portion dissolved and, on standing, yellowish, very thin leaflets, melting from 230° to 260°, separated out.

The original alcoholic filtrate containing all the gummy hydrazides from fraction II, except a small amount that was mentioned under fraction I, gave back, on hydrolysis, 15 grams of gum; 0.3 gram of this required 21.4 cc. 0.1 N potassium hydroxide for neutralization. The remainder was accordingly heated with 41.3 grams brucine and on crystallizing the salts obtained, first from ethyl alcohol and finally from methyl alcohol, a total of 32.35 grams, in three crops, of crystalline brucine salts melting from 90° to 115° were obtained (see p. 419); the noncrystalline brucine salts gave back, with sodium hydroxide, etc., 10.5 grams of acid gums which, on digesting 10 hours with an excess of quinine and water, took up 20 grams of this alkaloid. On crystallizing the salts obtained from a small amount of water, only 0.55 gram crystalline substance, melting at 160° (which was later worked up for *l*-glycerinic acid), separated out. The aqueous filtrate, after removing some polygalactonic lactone by dissolving in absolute alcohol, etc., gave back with sodium hydroxide 7 grams unidentified gum, from which, on further treatment with brucine, no crystalline salts could be obtained (see below).

Finally, the 27.1 grams low-melting brucine salts obtained from fraction D gave, with sodium hydroxide, 6 grams of gum which, when digested for 10 hours with water and quinine, took up 11 grams of the alkaloid, but no crystalline salts could be obtained by dissolving in water or alcohol. After removing some polygalactonic lactone in the usual manner, 4 grams of acid gum was recovered. This was converted into salts by digesting with 8.8 grams of brucine, but on crystallization from methyl alcohol only 1.22 grams of *d*-talonic brucine salt, melting at 150°, was obtained. The gummy

[1] Ber. d. chem. Ges., **35**, 3688.

brucine salts, decomposed with sodium hydroxide, etc., gave back 3.4 grams of gum which, on treatment with phenylhydrazine and alcohol, gave 0.6 gram *d*-galactonic hydrazide, melting from 195° to 198°. The noncrystalline soluble hydrazides were now combined with a similar mixture obtained from gum F, above, and gave, on hydrolysis, 5.2 grams unidentified gum (see below).

d-*Talonic Brucine.*—Three fractions of *d*-talonic brucine are referred to in the preceding pages, namely: 1.22 grams, melting at 150°; 2.45 grams melting at 150°; and 4.4 grams melting at 156°. These were obtained from gummy hydrazides soluble in alcohol and show very clearly that *d*-talonic acid, when treated with phenylhydrazine and alcohol (even when alone, as proved by an experiment with a synthetic product), is never precipitated completely as the phenylhydrazide. Fischer gives the melting point of *d*-talonic brucine at 130°–133°. I have found that this salt, when crystallized from its weight of water mixed with six times its weight of absolute alcohol, has, when air-dry, the melting point given by this investigator, but that on drying *in vacuo* it loses about 10 per cent. in weight and the melting point then goes up to 154°–156°. The combined three fractions of *d*-talonic brucine just mentioned, 8.07 grams, gave with sodium hydroxide, etc., 2.1 grams of acid gum which, mixed with 2.1 cc. each of alcohol and phenylhydrazine, gave 2.4 grams crude *d*-talonic phenylhydrazide well washed with cold alcohol; since a preparation of pure synthetic *d*-talonic acid gum was found to give only 75 per cent. of the theoretical amount of hydrazide on similar treatment, it is obvious that practically pure *d*-talonic acid was present.

The 32.35 grams of brucine salts, in three crops, melting between 90° and 115°, referred to on p. 418, gave, with sodium hydroxide, etc., 7.6 grams of gum which, on digestion with an excess of quinine and water for 10 hours, took up 13.1 grams of alkaloid. No crystalline salts could be obtained, and after the removal of some polygalactonic lactone, the quinine was split off with sodium hydroxide and 5.5 grams of acid gum recovered. This, on treatment with 12 grams of brucine and

crystallization of the resulting salts from alcohol, gave 8.9 grams of brucine salts melting at 138°; the remaining gummy brucine salts, decomposed with sodium hydroxide, etc., gave 2 grams of gum which, with phenylhydrazine and alcohol, gave 0.3 gram *d*-galactonic hydrazide melting at 195°. The 8.9 grams of crystalline salts gave back 2 grams of gum which, on similar treatment, gave 1.0 gram of *d*-talonic hydrazide, melting between 150° and 160°. The gummy soluble hydrazides from these two fractions gave back, on hydrolysis, 3 grams of unidentified gum (see below).

Unidentified Acid Gums from the Low-melting Brucine Salts.—The total amount of unidentified acid gums obtained finally from the various gummy brucine and quinine salts, as well as from gummy hydrazides, in the operations with the 157 grams of low-melting brucine salts described in the preceding pages, was 18.5 grams. These were now separated into 10.5 grams, I, soluble in acetic ether, and 8 grams, II, soluble in absolute alcohol. The amount of glycerinic acid present in I was now determined as directed by Nef;[1] 0.45 gram gave, with concentrated hydriodic acid, etc., 0.18 gram β-iodpropionic acid melting from 81° to 83°; hence about 40 per cent. of this material consists of glycerinic acid. This was also confirmed by taking 9.0 grams of the gum, I, and treating it, on the basis of a titration, with 32.2 grams brucine, etc.; on crystallizing the salts from alcohol, 19 grams melting from 190° to 205°, besides 2.22 grams melting from 120° to 130°, were obtained. The presence of *d*-erythronic acid in traces in this 19 gram portion of high-melting salts was subsequently established by experiment (see below). The 2.22 grams low-melting salt, decomposed with sodium hydroxide, gave 0.6 gram gum which, treated with phenylhydrazine and alcohol, gave 0.4 gram *d*-talonic hydrazide melting at 153°–156°. Finally, the alcoholic filtrate containing the gummy brucine salts gave back with sodium hydroxide, etc., 4.2 grams of acid gum which was united with gum II, 8 grams, after freeing the latter from tar as follows: Acylation for 8 hours at 100° with three parts of acetic anhy-

[1] Ann. Chem. (Liebig), **357**, 263.

dride gave only a relatively small amount of acylated gum soluble in hot ether which, on threefold hydrolysis, gave 3.25 grams of gum. The total amount of unidentified gum was therefore now 7.45 grams which, by means of hot acetic ether, was separated into 3.4 grams, soluble in this solvent, and 3.25 grams insoluble gum. The former, treated with 11.3 grams of brucine, etc., gave 2.63 grams of crystalline brucine salts melting at 202°. But no further crystalline salts could be obtained from either fraction; they were, therefore, finally discarded. The 2.63 grams high-melting brucine salt was not worked up further. It is evidently the same in character as the 19 gram portion mentioned above, which was subsequently proved to contain small amounts of *d*-erythronic acid.

II. l-*Threonic*, d-*Erythronic*, d,l-*Glycerinic Acids from the High-melting Brucine Salts.*—A preliminary attempt to separate the 70.75 grams, in two crops of 37.5 grams and 33.2 grams, respectively, from fractions A and B, of brucine salts melting between 206° and 208° soon showed that *d,l*-glycerinic acid was being split into its components, as described by Neuberg.[1] I repeated part of his work and obtained, in general, similar results. But on the whole I have found brucine less satisfactory than quinine, as used by Nef, in separating *d,l*-glycerinic acid into its components.

On the Resolution of d,l-*Glycerinic Acid into Its Optical Components.*—Ten grams of *d,l*-glycerinic acid gum (made from Kahlbaum's calcium glycerinate after crystallizing twice from water) was digested for 10 hours on the boiling water bath with water and 34.35 grams of quinine; complete solution took place and on concentrating to about 100 cc. a mass of crystalline needles separated out after standing 12 hours. These, when filtered, washed with 50 cc. water and dried on a porous plate, weighed 22.05 grams and melted at 178°. On recrystallization from 40 cc. hot water, 14.7 grams of the anhydrous salt, melting at 183°, was obtained. Ten grams of this, decomposed with sodium hydroxide, etc., gave 2 grams of acid gum. On digesting the gum with 300 cc. acetic ether,

[1] Ber. d. chem. Ges., **37**, 340.

1.65 grams dissolved. I have always found that a portion of the glycerinic acid gum remains insoluble but that the greater part is very easily soluble in this solvent. The soluble portion was now converted into the calcium salt which, on concentration of its solution to 10 cc. and subsequent addition of 10 cc. alcohol, gave 0.55 gram of salt melting at 138° and having a specific rotation of only +3°.70 for the hydrated salt, which corresponds to[1] +4°.08 for the anhydrous salt. The mother liquor, however, on concentration to 4 cc. and addition of 8 cc. alcohol, gave a second crop of practically pure *l*-glycerinic calcium, 1.2 grams, melting at 138°, and giving $[\alpha]_D^{20} = +14°.07$[1] for the hydrated salt, which corresponds to $[\alpha]_D^{20} = +15°.53$ for the anhydrous salt: $d = 1.011$; $p = 4.01$, *i. e.*, 0.8038 gram substance dried *in vacuo* and 19.2586 grams of water; $[\alpha]$ in a 1 dcm. tube = +0°.57.

l-*Glycerinic Brucine.*[2]—The 1.1 grams of *l*-glycerinic calcium, $[\alpha]_D^{20} = +14°.07$, mentioned above, was converted in the usual manner into 0.75 gram *l*-glycerinic acid gum, which, treated with 2.78 grams of brucine, etc., gave, from 63 cc. absolute alcohol, 2.35 grams of pure anhydrous *l*-glycerinic brucine in heavy transparent crystals, melting at 222°; the specific rotation at 20° was found to be —22°.02; $d = 1.011$; $p = 3.962$, *i. e.*, 0.7710 gram substance dried *in vacuo* and 18.6886 grams of water; found $[\alpha]$ in a 1 dcm. tube = —0°.882.

d-*Glycerinic Quinine.*—The aqueous filtrate from the 22.05

[1] Cf. Frankland: J. Chem. Soc., **63,** 297; also Fischer: Ber. d. chem. Ges., **40,** 1069–1070. The highest rotation given by Fischer for hydrated glycerinic calcium is +14°.5 in 4.6 per cent. concentration.

[2] The absolute space formula of *l*-glycerinic acid has been determined by Neuberg (Z. physiol. Chem., **44,** 145) as being

that of the so-called *l*-lactic acid, whose salts are dextrorotatory, is probably

furthermore, the absolute space formula of *d*-malic acid must be represented by

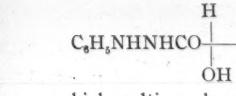
because it is formed by the reduction of *d*-tartaric acid with hydriodic acid (cf. Bremer: Ber. d. chem Ges., **8,** 1594, and **13,** 352).

grams of *l*-glycerinic quinine mentioned above gave, on distilling off the water at reduced pressure, 17.5 grams of quinine salt which, dissolved in 35 cc. absolute alcohol, gave 9.45 grams *d*-glycerinic quinine melting between 187° and 188°. This, crystallized once more from 37 cc. absolute alcohol, gave 6.6 grams of anhydrous *d*-glycerinic quinine in the form of crystalline needles with no change in the melting point; the specific rotation at 20° was found to be —126°.58; d = 1.011; p = 4.004, *i. e.*, 0.7746 grams substance and 18.5688 grams water; found $[\alpha]$ in a 1 dcm. tube = —5°.124.

The 6.6 grams quinine salt was now converted into the free acid and then into the calcium salt; the latter gave from 15 cc. each of water and alcohol 1.7 grams *d*-glycerinic calcium melting at 136°. The specific rotation of this salt at 20° was found to be only —10°.20, which shows that a small amount of the racemate was still present; d = 1.011; p = 4.004, *i. e.*, 0.6205 gram substance and 14.8749 grams of water; found $[\alpha]$ in a 1 dcm. tube = —0°.413.

d-*Glycerinic Brucine.*—The 1.7 grams calcium *d*-glycerinate, $[\alpha]_D^{20}$ = —10°.20, gave, on treatment with 0.66 gram oxalic acid, etc., 1.1 grams of the free acid which was converted by means of 4 grams of brucine into a salt; this, crystallized from 2.5 cc. water and 25 cc. absolute alcohol, gave a large amount of crystalline plates melting at 222°. These lost no weight over sulphuric acid *in vacuo* and gave a specific rotation of —33°.2 at 20°; d = 1.011; p = 3.992, *i. e.*, 0.6986 gram substance and 16.8006 grams of water; found $[\alpha]$ in a 1 dcm. tube = —1°.34.

l-*Threonic Acid Phenylhydrazide,*



high-melting brucine salts (in two crops), referred to above, in 35 cc. water and 350 cc. absolute alcohol, 32.1 grams of crystals melting from 212° to 213° separated out within two hours; these, on recrystallization from 16 cc. water and 160 cc. absolute alcohol, gave 16.4 grams salt with no change

in melting point; the latter finally gave, with sodium hydroxide, etc., 3.9 grams of gum which, on standing in the cold with 4 cc. each of alcohol and phenylhydrazine, gave 2.75 grams of crude *l*-threonic phenylhydrazine, melting at 155° after washing well with cold alcohol. Recrystallized from 75 cc. absolute alcohol, this gave 1.95 grams of transparent rhombic plates, melting at 158°, and the filtrate, concentrated to 20 cc., gave a second crop, 0.35 gram, with the same melting point. An analysis and optical investigation gave the following result:

0.1891 gram, dried *in vacuo*, gave 0.3686 gram CO_2 and 0.1144 gram H_2O.

0.1694 gram gave 19.5 cc. N at 20° and 744.4 mm.

	Calculated for $C_4H_{10}O_4N_2$.	Found.
C	53.10	53.11
H	6.19	6.72
N	12.40	12.88

$d = 1.012$; $p = 4.68$, *i. e.*, 1.0122 grams substance and 20.5940 grams of water; found $[\alpha]$ in a 2 dcm. tube = —2°.953, whence $[\alpha]_D^{20} = -31°.17$. The value given by Nef,[1] —26°.88, is too low, owing to an error on my part in calculating the concentration and also the density; that determination corrected was: $d = 1.012$; $p = 4.56$, *i. e.*, 0.7180 gram substance and 15.1141 grams water; found $[\alpha]$ in a 2 dcm. tube = —2°.86, whence $[\alpha]_D^{20} = -30°.98$.

The Brucine Salt of l-Threonic Acid.—Two and three-tenths grams *l*-threonic hydrazide, on hydrolysis, gave 1.05 grams of lactone gum and an optical determination gave: $d = 1.011$; $p = 4.00$, *i. e.*, 1.05 grams substance and 25.20 grams of water; found $[\alpha]$ in a 2 dcm. tube = —2°.42, whence $[\alpha]_D^{20} = -29°.9$. The specific rotation of various preparations of *l*-threonic lactone gum was, however, in different cases found to vary between —20° and —30°. On treating the 1.05 grams crude lactone, just referred to, with 3.5 grams of brucine and crystallizing the resulting salt from water and alcohol, 2.5 grams of long, narrow crystalline plates melting at

[1] Ann. Chem. (Liebig), **357**, 235.

213° to 214° were obtained. These, dissolved again in 2.5 cc. water and 25 cc. hot absolute alcohol, gave 2.1 grams of transparent plates, melting from 213° to 214°. An optical determination gave: $d = 1.011$; $p = 3.98$, *i. e.*, 0.9401 gram substance dried *in vacuo* and 22.6674 grams of water; found $[\alpha]$ in a 2 dcm. tube = —2°.61, whence $[\alpha]_D^{20} = -32°.40$.

The space formula of *l*-threonic acid was now determined by its almost quantitative transformation by oxidation to *l*-tartaric acid: 0.8 gram of the lactone was heated for 44 hours at 50°–60° with 4.2 grams of nitric acid (sp. gr. 1.228). On distilling off the excess of nitric acid under 15–30 mm. pressure (outside bath finally at 100°), 0.8 gram of a partly crystalline residue was left in the distilling flask. This, digested for six hours on the boiling water bath with 1.5 grams of powdered calcium carbonate and 600 cc. water, took up half a gram of calcium carbonate and only 0.05 gram calcium oxalate was found with the excess of calcium carbonate. The aqueous filtrate, concentrated to 50 cc., gave 0.85 gram very small, transparent crystals; these required 350 cc. boiling water for solution and gave, on treatment with 0.39 gram crystallized oxalic acid, etc., a crystalline acid, which, when dissolved in 40 cc. acetone, filtered and allowed to evaporate in an open dish, left 0.25 gram crystals of *l*-tartaric acid, melting at 169°–170°. This was proved as follows: An optical investigation gave: $d = 1.012$; $p = 3.013$, *i. e.*, 0.2448 gram substance and 7.8786 grams of water; found $[\alpha]$ in a 1 dcm. tube = —0°.435, whence $[\alpha]_D^{20} = -14°.26$. On converting the free acid back to the lime salt, etc., this gave the following results on analysis:

0.2261 gram air-dried salt, on ignition, left 0.0501 gram CaO.

	Calculated for $CaC_4H_4O_6.4H_2O$.[1]	Found.
Ca	15.38	15.83

A preparation of pure *d*-tartaric acid, recrystallized as directed above for the *l*-compound, melted at 169°–170°, and an optical determination gave: $d = 1.012$; $p = 3.058$, *i. e.*,

[1] Anschütz: Ann. Chem. (Liebig), **226**, 201.

0.9992 gram substance (dried *in vacuo*) and 31.7000 gram of water; found $[\alpha]$ in a 2 dcm. tube = +0°.988, whence $[\alpha]_D^{20}$ = +15°.96. The acid obtained by me from the oxidation of *l*-threonic acid lactone was therefore obviously the antipode, *l*-tartaric acid.

d- *and* l-*Glycerinic Acid by the Action of Fehling's Solution on Galactose.*—The alcoholic filtrate from the 2.75 grams of *l*-threonic hydrazide, mentioned above, which contained the alcohol-soluble and gummy acid phenylhydrazides, gave back, on hydrolysis, 2 grams of gum. This was united with 12.2 grams of acid gum obtained from the main portion of the 70.75 grams of high-melting brucine salts and another fraction, 10.4 grams, of high-melting brucine salts from fraction D (see above summary), by the action of sodium hydroxide, etc. The combined acid gums were boiled in aqueous solution with an excess of powdered quinine in the usual way and the salts obtained, on crystallization from water, gave 8.9 grams of *l*-glycerinic quinine, melting from 160° to 175°. The remaining quinine salts, easily soluble in cold water, then gave, on crystallization from absolute alcohol, 6.25 grams of salt melting at 160°. This, on treatment with sodium hydroxide, etc., gave 2 grams of free acid from which were obtained, with 2 cc. alcohol and phenylhydrazine, 1.3 grams *l*-threonic phenylhydrazide, melting at 155°–158°, and 0.3 gram oxalyl phenylhydrazide, melting from 230° to 260°. The gummy, alcoholic soluble hydrazides, on hydrolysis, gave back 0.7 gram of acid gum, which was united with the acids obtained from the non-crystalline quinine salts.

The 8.9 grams of *l*-glycerinic quinine mentioned above gave with sodium hydroxide, etc., 2.3 grams of crude acid which, on conversion into the calcium salt and crystallization from water and alcohol, gave 2.4 grams of practically pure calcium *l*-glycerinate, as shown by the following: An optical determination gave: d = 1.011; p = 4.008, *i. e.*, 0.3396 gram substance, dried *in vacuo*, and 8.1326 grams of water; found $[\alpha]$ in a 1 dcm. tube = +0°.55, whence $[\alpha]_D^{20}$ = +13°.57 for the hydrated salt.

0.3858 gram salt, on ignition, left 0.0769 gram CaO.

	Calculated for $Ca(C_6H_9O_4)_2.2H_2O$.	Found.
Ca	13.99	14.23

The acids recovered from the gummy quinine salts and hydrazides amounted in all to 9.2 grams; these, on acylation, gave 11 grams of acylated gums soluble in ether. These were separated by means of aqueous soda solution and ether, as directed by Nef,[1] into 6.3 grams acylated glycerinic acid and 2.15 grams of neutral acylated threonic and erythronic lactones. The acylated glycerinic acid, on threefold hydrolysis, gave 4 grams of acids; 0.45 gram of this, on treatment with concentrated hydrogen iodide, as directed by Nef,[2] gave 0.40 gram β-iodpropionic acid melting from 81° to 83°. Hence, practically only glycerinic acid was present in this portion. The remainder, 3.5 grams, on conversion into the calcium salt, gave, by crystallization from water, 2.1 grams glycerinic calcium melting at 135°, and, by precipitation with alcohol, 2.5 grams of lime salts. The former was found to be optically inactive and on analysis gave the following result:

0.2434 gram, dried *in vacuo*, left, on ignition, 0.0469 gram CaO.

	Calculated for $Ca(C_3H_5O_4)_2.2H_2O$.	Found.
Ca	13.99	13.77

The 2.5 grams of precipitated calcium salts, united with one gram of an analogous calcium salt, mentioned below, was found to lose about 10 per cent. in weight on drying over sulphuric acid *in vacuo*. An optical determination and analysis then gave:

0.2594 gram, dried *in vacuo*, left, on ignition, 0.0484 gram CaO.

	Calculated for $Ca(C_3H_5O_4)_2.2H_2O$.	Found.
Ca	13.99	13.34

$d = 1.011$; $p = 4.016$, *i. e.*, 0.4032 gram substance and 9.6362 grams of water; found $[\alpha]$ in a 1 dcm. tube = —0°.13, whence $[\alpha]_D^{20} = -3°.20$. This was probably a mixture,

[1] Ann. Chem. (Liebig), **357**, 239–240.
[2] *Loc. cit.*

mainly of *d*- and *l*-glycerinic calcium, containing small amounts of *l*-threonic and *d*-erythronic calcium, as proved by a further study of its behavior towards dilute nitric acid (see below).

The above mentioned 2.15 grams of neutral acylated threonic and erythronic lactones, on hydrolysis, gave 1.1 grams of gum; this, on mixing with 1.1 cc. alcohol and phenylhydrazine, gave 0.25 gram *l*-threonic hydrazide melting at 155°. The gummy, alcohol-soluble hydrazides, on hydrolysis, gave back 0.7 gram of acid which, when converted into the lime salt and precipitated by alcohol, gave one gram of salt which, before analysis, was united with the 2.5 grams of lime salts mentioned above.

On the Presence of d-*Erythronic Acid in the Nonvolatile Gums Obtained from* d-*Galactose by Fehling's Solution.*—It is apparent, from the properties of free *d*-erythronic lactone, its hydrazide, and the brucine salt, as ascertained by Ruff,[1] that traces of this acid might easily escape detection in the presence of large amounts of *d,l*-glycerinic acid. The brucine salt of *d,l*-erythronic acid, prepared from the pure *d,l*-lactone[2] and brucine, can easily be resolved into its optical components, as I have found,[3] by crystallization from its weight of water and twice its weight of absolute alcohol. Thus, I obtained from *d,l*-erythronic brucine, which in four per cent. concentration gave $[\alpha]_D^{20} = -26°.52$, by crystallization, as directed, *d*-erythronic brucine, which gave $[\alpha]_D^{20} = -23°.42$; $d = 1.011$; $p = 3.99$, *i. e.*, 0.9913 gram substance dried *in vacuo* and 23.8349 grams of water; found $[\alpha]$ in a 2 dcm. tube $= -1°.89$. From this brucine salt I obtained *d*-erythronic lactone, melting from 92°–93° and containing some of the *l*-form, as is obvious from the following: The specific rotation was found to be only —23°.1 instead of —73°.3, given for the pure substance by Ruff; $d = 1.010$; $p = 2.95$, *i. e.*, 0.3682 gram dried *in vacuo* and 12.0746 grams of water; found $[\alpha]$ in a 1 dcm. tube $= -0°.69$. On treatment with phenylhydrazine and alcohol I obtained from it considerable

[1] Ber. d. chem. Ges., **32**, 3678.
[2] Nef: Ann. Chem. (Liebig), **357**, 248.
[3] Cf. also Lespieau: Compt. Rend., **144**, 144–146; Bull. Soc. Chim., [4] **1**, 1117.

d,l-erythronic hydrazide[1] melting at 150°, as well as some pure *d*-erythronic hydrazide[2] melting at 126° to 127° and having a specific rotation of —21°; *d* was not determined but taken as unity; $p = 0.89$, *i. e.*, 0.0812 gram of substance dried *in vacuo* and 8.9774 grams of water; found $[\alpha]$ in a 1 dcm. tube = —0°.19. The experiments just described prove very sharply the correctness of the conclusions of Nef,[3] namely, that it is easily possible to recognize the presence of racemic (*d,l*-) erythronic lactone, as well as to determine the presence of an excess of one of its optical components, by the phenylhydrazine treatment.

The presence of erythronic lactone in my Fehling's solution mixture was now established as follows: In the first place it was proved by experiment that 3.8 grams of *d*-tartaric acid heated for 36 hours in a bath kept between 60° and 65° with five times its weight of nitric acid, sp. gr. 1.228, remained entirely unchanged. Secondly, one gram of *d,l*-erythronic lactone melting at 92°–93° was oxidized with five times its weight of nitric acid, sp. gr. 1.218, at 55° to 65°, for 41 hours, *i. e.*, until the evolution of brown fumes had ceased; on distilling the volatile products at 20 mm. pressure, finally at 100°, 1.15 grams of crystalline residue remained. This, by treatment with an excess of powdered calcium carbonate, was converted into 0.12 gram calcium oxalate and 1.62 grams of calcium mesotartrate, $CaC_4H_4O_6.3H_2O$, obtained in the form of large transparent cubical crystals.[4] It is evident, therefore, from the facts presented above that *l*-threonic, as well as *d*- and *l*-erythronic acids, are oxidized almost quantitatively to the corresponding tartaric acids under the conditions described. Finally, *d,l*-glycerinic gum, when oxidized in a similar manner with nitric acid, sp. gr. 1.218, gave, besides a large amount of oxalic acid, much yellowish gummy material whose calcium salt was also yellow and very soluble in water. It is therefore clear, by application of the above data and by use of the previous observa-

[1] Nef: Ann. Chem. (Liebig), **357**, 250.
[2] Ruff: Ber. d. chem. Ges., **32**, 3678.
[3] Ann. Chem. (Liebig), **357**, 234–5.
[4] Cf. Holleman: Rec. Trav. Chim., **17**, 72.

tions of Nef, that the nature of the mixture of high-melting brucine salts obtained by the action of Fehling's solution on hexoses can now be pretty accurately ascertained quantitatively.

Accordingly, 19 grams of unidentified brucine salts from galactose, melting from 190° to 205° and consisting only of threonic, erythronic and glycerinic acids, now gave back, with sodium hydroxide, etc., 3.8 grams of acid gums. These, when oxidized with 5 parts of nitric acid, sp. gr. 1.218, for 40 hours, at 55° to 65°, gave, after removal of volatile products under 20 mm. pressure, finally at 100°, 3.35 grams of yellowish pasty material filled with crystals of oxalic acid. This was resolved, by treatment in aqueous solution with an excess of powdered calcium carbonate, into 1.6 grams calcium oxalate and 1.7 grams very soluble yellowish calcium salts, both obviously oxidation products of glycerinic acid; and finally into 0.58 gram calcium mesotartrate crystallizing in transparent cubes which gave the following results on analysis:

0.1462 gram of air-dry salt, on ignition, gave 0.0338 gram CaO.

	Calculated for $CaC_4H_4O_6.3H_2O$.[1]	Found.
Ca	16.55	16.52

Finally, 2.6 grams of the crude precipitated and analyzed calcium glycerinate, mentioned above as containing a small amount of trioxybutyrate of calcium, gave back, on treatment with the calculated amount of oxalic acid, etc., 2 grams of acid gum; this, on oxidation with 5 parts nitric acid in the usual manner, gave 1.6 grams of yellowish, partly crystalline residue. Treatment of the oxidation products with an excess of powdered calcium carbonate gave 1.05 grams calcium oxalate and 0.15 to 0.20 gram of pure calcium mesotartrate in transparent cubes, besides some yellow, easily soluble calcium salts.

These experiments, therefore, establish beyond doubt the presence of very small amounts of erythronic acid in the mixture of nonvolatile acids obtained from galactose and

[1] Kekulè and Anschütz: Ber. d. chem. Ges., **14**, 716–717.

Fehling's solution. Furthermore, the product present must be either *d*- or *l*-erythronic lactone and not the racemic form because *d,l*-erythonic lactone can easily be identified by its very difficultly soluble and high-melting hydrazide.[1] Finally, since optically active *l*-threonic lactone is formed and in relatively much larger amount, and the theory presented in the first part of this paper calls for the *d*-modification, I consider it in the highest degree probable that *d*-erythronic lactone in traces was the actual reaction product.

Summarizing, in conclusion, my results, I have obtained from 118 grams of *d*-galactose: 2.49 grams of carbon dioxide, 15.69 grams of formic acid and 102.1 grams of nonvolatile oxy acids; from the latter I have actually isolated 13 grams of *d*-galactonic acid, 5.33 grams *d*-talonic acid, 0.5 gram oxalic acid, 2.58 grams *l*-threonic lactone, traces of *d*-erythronic lactone, about 11 grams of *d,l*-glycerinic acid, and 11.75 grams of glycollic acid. A rough estimate of the relative amount of the various components present in the 102 grams nonvolatile gums obtained is as follows: glycollic acid, 20 to 30 grams; glycerinic acid, 20 to 30 grams; trioxybutyrolactones, 4 to 8 grams; hexonic acids, 20 to 30 grams.

In conclusion, I want to thank Dr. Nef for his continued help and encouragement in the course of this work.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXXII.—RESEARCHES ON PYRIMIDINES: THE ACTION OF METHYL IODIDE AND OF BENZYL CHLORIDE UPON 2-OXY-4-METHYL-6-METHYL-MERCAPTOPYRIMIDINE.[2]

[FORTY-SEVENTH PAPER.]

By Henry L. Wheeler and David F. McFarland.

The papers so far published on the alkylation of mercaptopyrimidines, with but one exception, have been confined to a description of the results obtained from a study of 2-mer-

[1] Nef: Ann. Chem. (Liebig), **357**, 250.

[2] Part of a thesis presented by David F. McFarland for the degree of Ph.D., Yale, 1909.

capto-6-oxypyrimidines. In most cases 2-mercapto-6-oxypyrimidines were found to alkylate both in the 1- and, more or less, in the 3-position.[1]

In the exception mentioned, Wheeler and Johnson[2] showed that when a compound having the opposite configuration, the mercapto group and the oxygen atom being interchanged, 2-oxy-6-methylmercaptopyrimidine for example, was treated with potassium hydroxide and either methyl iodide or benzyl chloride, 3-alkyl derivatives were obtained. No 1-derivative was observed in this particular alkylation. Since the 3-alkyl-6-mercapto derivatives pass quantitatively into the 3-alkyl compounds of uracil when boiled with hydrochloric acid, this procedure is therefore the best for the preparation of these compounds.

With this result at hand, it then became a question whether or not 2-oxy-6-mercaptopyrimidines in other cases or in general would be the best to select for the preparation of 3-alkyl derivatives. Cytosine, or 2-oxy-6-aminopyrimidine, which has a constitution analogous to these 2-oxy-6-mercaptopyrimidines, also gives the 3-alkyl derivative on methylation.[3]

It seems to us that any new facts in regard to methods which lead to the formation of 3-alkyl derivatives or 3-attachments are of interest since results have been obtained by Johnson and Clapp[4] which can be explained by the assumption that uracil, thymine, and cytosine are substituted or attached to other groups in these positions in the nucleic acids.

In our preceding paper we have shown that 2-methylmercapto- and 2-ethylmercapto-4-methyl-6-oxypyrimidine give 1-alkyl derivatives, the formation of the isomeric 3-derivatives in these cases not being observed. It was therefore of especial interest, in the above connection, to study, in this case, the alkylation of the compound having the opposite configuration, namely, 2-oxy-4-methyl-6-methylmercapto-

[1] For a list of these papers see THIS JOURNAL, **42**, 30 (1909).
[2] *Ibid.*
[3] Johnson and Clapp: J. Biol. Chem., **5**, 163 (1908).
[4] *Loc. cit.*

pyrimidine. This has now been done and we find that this pyrimidine, with methyl iodide and benzyl chloride, not only gives 3-alkyl derivatives but also the isomeric 1-compounds. In the case of the action of methyl iodide, the 1- and 3-isomers are formed in about equal proportions. Benzyl chloride gave more of the 3- than of the 1-benzyl compound.

The presence of a mercapto group or the absence of oxygen in the 6-position therefore appears to favor the formation of 3-alkyl derivatives. There is, however, no strict regularity in these alkylations, so that in new cases it is impossible to predict whether a 1- or 3-derivative, or a mixture of both, will result.

The starting point for the present work was the preparation of List's[1] 2-thio-4-methyluracil (I) from acetoacetic ester and thiourea. This gave 2-methylmercapto-4-methyl-6-oxypyrimidine (II) by List's method of alkylation.

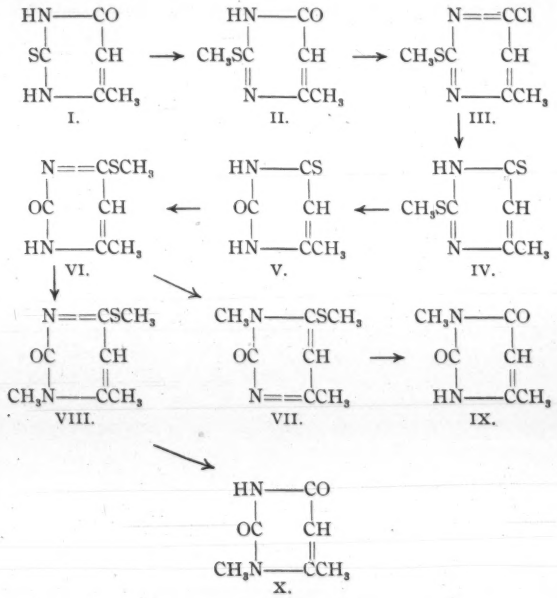
The new 2-methylmercapto-4-methyl-6-chlorpyrimidine (III) was then prepared by warming the material with phosphorus pentachloride and some oxychloride. When this compound was warmed with an excess of alcoholic potassium sulphhydrate, 2-methylmercapto-4-methyl-6-thiopyrimidine (IV) was obtained, and when the latter was boiled with hydrochloric acid 4-methyl-6-thiouracil (V) resulted.

The calculated quantity of sodium ethylate and methyl iodide then gave 2-oxy-4-methyl-6-methylmercaptopyrimidine (VI). An excess of potassium hydroxide and methyl iodide, in alcoholic solution, gave 2-oxy-3,4-dimethyl-6-methylmercaptopyrimidine (VIII) and 2-oxy-1,4-dimethyl-6-methylmercaptopyrimidine(?) (VII). The latter was not obtained in a state of purity but its presence in the oily fraction was indicated by the behavior of this fraction toward hydrochloric acid. When boiled with hydrochloric acid the compounds VII and VIII gave the corresponding dimethyluracils described by Behrend,[2] namely, 1,4-dimethyluracil (IX) and 3,4-dimethyluracil (X).

[1] Ann. Chem. (Liebig), **236**, 12 (1886).

[2] Behrend and Dietrich: Ann. Chem. (Liebig), **309**, 265 (1899). Behrend and Thurn: *Ibid.*, **323**, 160 (1902).

The formation of 1-alkyl derivatives in this reaction could be explained otherwise, without the assumption of the formation of the compound represented by formula VII, if 2-oxy-4-methyl-6-methylmercaptopyrimidine lost mercaptan during the alkylation. 4-Methyluracil being formed, 1-alkyl derivatives would result. However, we have treated 2-oxy-4-methyl-6-methylmercaptopyrimidine with alkali, under the same conditions as those in the alkylations, and we have found that no 4-methyluracil was formed. The mercapto compound was recovered unaltered. The various steps in the synthesis of these pyrimidines may, therefore, be represented as follows:



EXPERIMENTAL PART.

2-Methylmercapto-4-methyl-6-chlorpyrimidine,

.—Fifty grams of 2-methylmercapto-4-methyl-6-oxypyrimidine were moistened with phosphorus oxychloride in a distilling bulb and then one molecular proportion (66.8 grams) of phosphorus pentachloride was added. No action was observed in the cold, and even when the mixture was warmed the reaction began only very slowly. The mass slowly liquefied with a regular, quiet evolution of hydrogen chloride. After two hours warming, the liquefaction was complete and the evolution of gas was greatly diminished. The phosphorus oxychloride was removed by distilling under reduced pressure, and the oil which remained was poured on cracked ice. It solidified to a yellow solid, which was allowed to remain in the ice water for some time and then extracted with ether. The solution was dried with calcium chloride and, on evaporation, the oil obtained was distilled at 32–35 mm. pressure. The greater part (42.8 grams) boiled steadily at 147°. This is 77 per cent. of the calculated. On cooling, this fraction solidified and then melted at 39°–40°. The substance is very soluble in all of the common solvents. When dissolved in the smallest possible quantity of petroleum ether it separated in beautiful, long needles. These were pressed on filter paper and dried in a desiccator for analysis:

	Calculated for $C_6H_7N_2SCl$.	Found.
N	16.02	16.02

2-Methylmercapto-4-methyl-6-thiopyrimidine,

.—Ten grams of the above chlorpyrimidine were mixed with an alcoholic solution of potassium hydrosulphide, made by saturating a solution of 19.2 grams of potas-

sium hydroxide in 60 cc. of alcohol with hydrogen sulphide. The chlor compound dissolved and very soon crystals of the potassium salt of 2-methylmercapto-4-methyl-6-thiopyrimidine began to separate. The mixture was warmed for half an hour on the steam bath and the alcohol was then evaporated. The residue dissolved almost completely in water and the solution was filtered from a slight reddish sediment. On acidifying with dilute acetic acid, the free thio compound was precipitated. The quantity obtained (9.85 grams) agreed almost exactly with the theoretical yield. This substance is very difficultly soluble in boiling water, from which it separates in light yellow, minute needles. It dissolves easily in ammonium hydroxide and separates again when the ammonia is boiled off. It is unstable in aqueous alkali and the solution takes on a dark red color. Dilute alcohol or water should therefore not be used in its preparation. Alcohol dissolves it with some difficulty, giving needle-like prisms. On standing, the alcoholic mother liquors take on a deep red color.

	Calculated for $C_6H_8N_2S_2$.	Found.
N	16.27	16.12

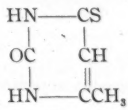
2-Methylmercapto-4-methyl-6-thiopyrimidine exhibited a characteristic behavior when heated, the product obtained at high temperatures being 2,6-dithio-4-methyluracil. This substance has been described by Gabriel and Colman.[1] When slowly heated, such as is commonly done in taking melting points, it partially melted, like a mixture, at 212° to a milky mass, which effervesced on further heating and then solidified. If the tube was placed in a bath already heated to 200° and the temperature rapidly raised, it then melted completely to a clear yellow oil at 214°. A slight elevation of temperature caused the oil to effervesce and finally solidify to a crystalline solid. On further heating this solid grew red, the color deepening until the material melted or decomposed to a red-brown oil at 280°–290°.

One gram of the mercapto-6-thiopyrimidine was heated for

[1] Ber. d. chem. Ges., **32**, 2921 (1899).

a short time at 215°–223°. The product was treated with hot alcohol and the portion which did not dissolve was found to be also almost insoluble in boiling water. On heating, decomposition set in above 260°, but the material did not melt at 310°. A nitrogen determination gave 17.53 per cent. while the calculated for 2,6-dithio-4-methyluracil is 17.72 per cent.

6-Thio-4-methyluracil,

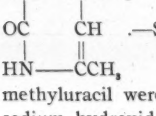


.—This compound is formed quantitatively by boiling 2-methylmercapto-4-methyl-6-thiopyrimidine with strong hydrochloric acid for several hours and then evaporating to dryness. Long heating is required to completely expel the mercaptan from the compound. The product is almost insoluble in alcohol and difficultly soluble in boiling water. It crystallizes in irregular, prismatic forms, has a sulphur-yellow color, but no definite melting point. When heated it decomposes above 250°.

	Calculated for $C_5H_6ON_2S$.	Found.
N	19.71	19.42

The sulphur in this compound is more firmly bound than that in 6-thiouracil or 6-thiothymine. It was not removed on long heating on the steam bath with hydrochloric acid.

2-Oxy-4-methyl-6-methylmercaptopyrimidine,



.—Seven and six-tenths grams of 6-thio-4-methyluracil were dissolved by warming with 2.2 grams of sodium hydroxide in 50 cc. of water and 30 cc. of methyl alcohol, and 8.5 grams of methyl iodide were added. The mixture was warmed until no further alkaline reaction was obtained. It was then evaporated to dryness. The product dissolved easily in water, leaving only a little oil, which was removed by filtration. On standing, pale yellow, flat, needle-

like crystals formed. The yield in one case was 83 per cent. of the calculated. When recrystallized from water the material melted at 174°–175° to a clear oil. The substance was very soluble in water and alcohol, and it had a tendency to form supersaturated solutions. On this account it crystallized from water only after standing for some time. It is not appreciably volatile with steam.

	Calculated for $C_6H_8ON_2S$.	Found.
N	17.94	17.67

Action of Benzyl Chloride.—Four grams of 2-oxy-4-methyl-6-methylmercaptopyrimidine were dissolved in alcohol with 1.45 grams of potassium hydroxide. To the cooled solution, 3.3 grams of freshly distilled benzyl chloride were added and the mixture was allowed to stand for several days. The reaction then still being incomplete, the mixture was warmed for two hours on the steam bath. Some potassium chloride which separated was filtered off and the solution was allowed to evaporate spontaneously. A small amount of solid remained, mixed with a larger quantity of red oil, which had a very pungent odor. When the mixture was spread on a porous plate the oil was absorbed, leaving 1.6 grams of the sticky solid. This was very soluble in alcohol and benzene and very difficultly soluble in water. From none of these solutions could a pure crystalline substance be obtained, so the crude solid was treated directly with hydrochloric acid.

One and a half grams of the solid were digested on the steam bath with a large excess of concentrated hydrochloric acid and then evaporated to dryness. This operation was twice repeated before mercaptan was completely eliminated. The residue weighed 1.1 grams. On crystallizing from alcohol it was found to consist principally of 4-methyluracil, decomposing at 265°–300°, and, by extracting the product with cold chloroform a very small amount of *1-benzyl-4-methyluracil* was obtained. The red oil, which was absorbed in a porous plate, was extracted with boiling alcohol and treated with concentrated hydrochloric acid as above. When mer-

captan ceased being evolved, the dry residue was stirred with alcohol. This left 1.1 grams of substance undissolved, while the red color of the residue was removed. When the material was crystallized once from alcohol, Hagen's *3-benzyl-4-methyluracil*, melting at 231°–232°, was obtained. The mother liquor appeared to contain a mixture of this compound and of the 1-benzyl derivative. We conclude from the above that of the two isomers the 3-benzyl derivative is formed in larger amount.

Action of Methyl Iodide; 2-Oxy-3,4-dimethyl-6-methylmercaptopyrimidine.—Four and three-tenths grams of potassium hydroxide were dissolved in 50 cc. of methyl alcohol and 4 grams of 2-oxy-4-methyl-6-methylmercaptopyrimidine were added. This dissolved at once without warming. Three molecular proportions (11 grams) of methyl iodide were then added and the mixture was allowed to stand two days. At the end of this time considerable potassium iodide had separated and the solution no longer gave an alkaline reaction. The alcohol was then evaporated under reduced pressure and the dry residue was extracted with three portions of boiling chloroform. On evaporation of the chloroform at ordinary temperatures, slightly yellow, large, prismatic crystals mixed with oil separated. The oil did not solidify on standing for some time. It was removed by absorption in filter paper and saved for later treatment (see below).

The crystals, which weighed 2.3 grams or 53 per cent. of the calculated for dimethyl-6-methylmercaptopyrimidine, were twice recrystallized from benzene. Some brownish color was removed by boiling the solution with animal charcoal, whereupon, on filtering, splendid prisms, somewhat irregular in outline, were obtained. They melted to a clear oil at 170°–171°, and were found to be very soluble in water and in alcohol, but only moderately so in benzene.

	Calculated for $C_7H_{10}ON_2S$.	Found.
N	16.47	16.53

This material was boiled with hydrochloric acid until it gave no test for sulphur. It was then crystallized twice from alcohol, whereupon it melted at 220° and agreed in proper-

ties with Behrend's 3,4-dimethyluracil. A nitrogen determination gave 20.06 per cent. nitrogen while the calculated for this compound is 20.00 per cent.

1,4-Dimethyl-2-oxy-6-methylmercaptopyrimidine (?).—This compound was not isolated in a pure state but its presence in the oil obtained above was indicated by the hydrolysis of the oil with strong hydrochloric acid. After digesting on the steam bath until mercaptan was no longer evolved, the solution was evaporated to dryness and the residue was crystallized from water. It separated in small prisms melting sharply, to a clear brown oil, at 260° and when mixed with a sample of β-dimethyluracil or 1,4-dimethyluracil the melting point was not lowered.

	Calculated for $C_6H_8O_2N_2$.	Found.
N	20.00	20.02

2-Oxy-4-methyl-6-orthonitrobenzylmercaptopyrimidine.—Molecular proportions of 6-thio-4-methyluracil, potassium hydroxide, and *o*-nitrobenzyl chloride were mixed in dilute alcoholic solution. The mixture was then warmed until it gave a neutral reaction. When the alcohol was evaporated and the residue was treated with water the yield of crude product agreed with the calculated amount. This material dissolved fairly easily in hot alcohol and, on cooling, it gave clusters of yellow, lancet-shaped crystals melting to a clear oil at 205°.

	Calculated for $C_{12}H_{11}O_3N_3S$.	Found.
N	15.16	15.24

2-Oxy-4-methyl-6-metadinitrophenylmercaptopyrimidine, prepared in a similar manner to the above, from 6-thio-4-methyluracil, potassium hydroxide, and 1-brom-2,4-dinitrobenzene, formed very small bunches of fine, mustard-yellow needles when crystallized from alcohol. It melted at 208°.

	Calculated for $C_{11}H_8O_5N_4S$.	Found.
N	18.18	18.05

NEW HAVEN, CONN.,
May, 1909.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXXIII.—RESEARCHES ON HALOGEN AMINO ACIDS: IODINE DERIVATIVES OF PARATOLUIDINE; 3,5-DIIOD-4-AMINOBENZOIC ACID.[1]

[SIXTH PAPER.]

By Henry L. Wheeler and Leonard M. Liddle.

In the year 1848 A. W. Hofmann[2] showed that aniline reacts directly with iodine and that *p*-iodaniline is formed. With the exception of some remarks by Losanitsch[3] and Mills,[4] on the possibility of higher iodated products being formed in this reaction, it appears that no further attention has been given to the subject since that time.

A search in the literature also failed to reveal any description of the direct action of iodine on the homologues of aniline. The iodine derivatives of the toluidines that have been described have been made by a more round-about method.

Willgerodt and Gartner[5] have prepared one of the two theoretically possible monoiod-*p*-toluidines, namely, 1-methyl-4-amino-2-iodbenzene, by reducing the corresponding nitro-iodtoluene.

One diiod-*p*-toluidine has been described. This was obtained by Michael and Norton[6] by the action of iodine monochloride on *p*-toluidine hydrochloride. It was assumed, but it was not proved, that iodine entered the positions adjacent to the amino group, the substance being considered as 1-methyl-3,5-diiod-4-aminobenzene. In the same manner *p*-aminobenzoic acid also gave a diiod derivative, which was represented as 3,5-diiod-*p*-aminobenzoic acid. Michael and Norton state: "The determination of the position of the iodine atoms in the above compounds will require a separate research. The weak basic properties of diiodaniline, and the

[1] Part of a thesis presented by Leonard M. Liddle for the degree of Ph.D., Yale, 1909.

[2] Ann. Chem. (Liebig), **67**, 61.

[3] Ber. d. chem. Ges., **5**, 157 (1872).

[4] Ann. Chem. (Liebig), **176**, 356 (1875).

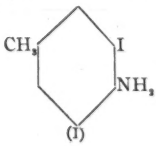
[5] Ber. d. chem. Ges., **41**, 2813 (1908).

[6] This Journal, **1**, 264 (1879); Ber. d. chem. Ges., **11**, 115 (1878).

absence of basic properties in triiodaniline, indicate that the second and third iodine atoms entering the molecules have taken the ortho position to the amino group, since among the numerous known di- and trichlor- and bromanilines, only those whose halogen atoms are in the ortho position to the amido group show a like loss of basic properties."

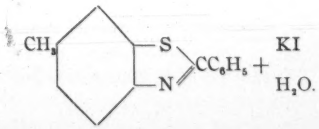
As the writer intends to use these diiod compounds in future work, it was necessary first of all to determine their structure. This was accomplished as follows: It was first found that *p*-toluidine reacts quite smoothly with two atomic proportions of iodine and that a monoiod-*p*-toluidine is formed. This substance, being different from the material obtained by Willgerodt and Gartner, must be 1-methyl-3-iod-4-amino-benzene (I).

That this new iodine derivative has the iodine adjacent to the amino group was proved by heating the substance with the potassium salt of thiobenzoic acid, whereupon an anhydro base was formed:



(I)

$$+ KS.COC_6H_5 =$$



$$+ KI + H_2O.$$

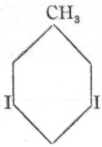
Hess[1] has previously prepared this anhydro base from "*p*-amidtoluol-*m*-sulphhydrat" and benzoyl chloride.

When this monoiod-*p*-toluidine is mixed with two atomic proportions of iodine, or when *p*-toluidine is treated with two molecules of iodine (I_4), in the presence of water and calcium carbonate, the diiod-*p*-toluidine described by Michael and Norton is easily obtained. Some dark-colored tar is

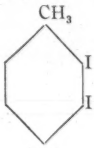
[1] Ber. d. chem. Ges., **14**, 493 (1881).

formed, but, nevertheless, the yield is good. We found among the by-products *p*-azotoluene. Our direct method is the best for the preparation of this diiodtoluidine.

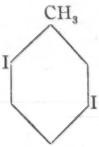
The diiodtoluidine, when diazotized in sulphuric acid solution and boiled with alcohol, gives a new diiodtoluene. Since one of the iodine atoms has been shown to be in the 3-position, this diiodtoluene must be one of the following new compounds:



(II)
M. p., 44°–45°.



(III)
M. p., 31°–32°.



(IV)
M. p., 30°–31°.

We have now also prepared the diiodtoluenes, 1-methyl-2,3-diiodbenzene (III) and 1-methyl-3,6-diiodbenzene (IV), and we find that when crystals of any two of these three substances are mixed the mixture immediately liquefies.

It is obvious, from this and other reasons, that we are dealing here with three different diiodtoluenes.

It therefore follows that the iodine atoms in diiod-*p*-toluidine (V) are in the 3,5-position. It may also be added that our diiodtoluene (II) from diiod-*p*-toluidine is not identical with any of the other diiodtoluenes already described.[1] Since the above three diiodtoluenes complete the list of the six theoretically possible isomers, it is to be concluded that no rearrangement has taken place in diazotizing.

1-Methyl-2,3-diiodbenzene (III) was prepared from 3-nitro-2-amino-1-methylbenzene.[2] This was converted into 2-iod-3-nitro-1-methylbenzene by diazotizing and treating the solution with potassium iodide. By reducing with ferrous sulphate and ammonia, 3-amino-2-iod-1-methylbenzene was obtained. The preparation of this compound completes the

[1] 2,6-Diiodtoluene; Cohen and Miller: J. Chem. Soc., **85**, 1627 (1904). 2,4-Diiodtoluene; Neumann: Ann. Chem. (Liebig), **241**, 51 (1887). 3,4-Diiodtoluene; Willgerodt and Simonis: Ber. d. chem. Ges., **39**, 269 (1906).

[2] Reverdin and Crépieux: Ber. d. chem. Ges., **33**, 2498 (1900).

list of the four theoretically possible monoamino derivatives of *o*-iodtoluene. This was again diazotized and with potassium iodide gave the 2,3-diiodtoluene (III).

2,5-Diiodtoluene or 3,6-diiodtoluene (IV) was prepared from 1-methyl-2-amino-5-iodbenzene[1] by replacing the amino group with iodine.

When the acetyl derivative of monoiodtoluidine prepared from *p*-toluidine and iodine is oxidized with potassium permanganate, 3-iod-4-acetylaminobenzoic acid is formed. The isomeric 2-iod-4-acetylaminobenzoic acid, on boiling with concentrated hydrochloric acid, gives, according to Willgerodt and Gartner, 2-iod-4-aminobenzoic acid. When our acetyliodamino acid was boiled with concentrated hydrochloric acid a curious result was obtained. The acetyl group was removed, to be sure, but instead of the expected monoiodamino acid a diiodamino acid was obtained, along with a corresponding amount of *p*-aminobenzoic acid. The main reaction took place as follows:

$$2C_6H_3.NHCOCH_3.I.COOH + 2H_2O = C_6H_2.NH_2.I_2.COOH + C_6H_4.NH_2.COOH + 2CH_3COOH.$$

A small amount of 3-iod-4-aminobenzoic acid, however, was obtained in one of these experiments. It was found later that this monoiodamino acid could be more easily obtained by the action of iodine monochloride on *p*-aminobenzoic acid.

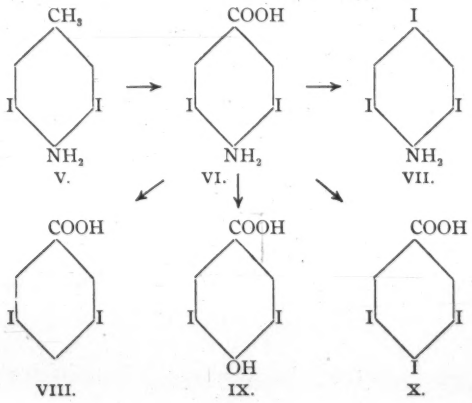
It may be added that 3-iod-*p*-acettoluide gave 3,5-diiod-*p*-toluidine on boiling with hydrochloric acid.

The diiodaminobenzoic acid formed in the above reaction proved to be identical with Michael and Norton's diiodaminobenzoic acid and was shown to be 3,5-diiod-4-aminobenzoic acid (VI) by oxidizing the acetyl derivative of 3,5-diiod-*p*-toluidine with potassium permanganate, the same acid being obtained. Michael and Norton's method is the best for the preparation of this acid.

When the potassium salt of 3,5-diiod-4-aminobenzoic acid was heated in aqueous solution with iodine, carbon dioxide was liberated and 2,4,6-triiodaniline was obtained. Iodine

[1] See following paper.

takes the place of the carboxyl group in this reaction. We have found, in this connection, that the potassium salt of *p*-aminobenzoic acid reacts in a similar manner with iodine, at ordinary temperature, giving *p*-iodaniline, and that no iodamino acid was obtained. From 3,5-diiod-*p*-aminobenzoic acid we have prepared, by diazo reactions, 3,4,5-triiodbenzoic acid (X), 3,5-diiod-*p*-hydroxybenzoic acid (IX), which is identical with the diiod-*p*-hydroxybenzoic acid obtained by Peltzer[1] by directly iodating *p*-hydroxybenzoic acid, and 3,5-diiodbenzoic acid (VIII), and in a following paper we will show that this diiodbenzoic acid is identical with 3,5-diiodbenzoic acid prepared from 3,5-dinitrobenzoic acid. This, therefore, settles the structure of these compounds.



EXPERIMENTAL PART.

*3-Iod-*p*-toluidine*, $C_6H_3\langle^{CH_3\,(1)}_{I\quad(3)}_{NH_2\,(4)}$.—When *p*-toluidine and iodine were mixed in molecular proportions the mixture fused to a dark oil. The action took place immediately, but in

[1] Ann. Chem. (Liebig), **146**, 294 (1868).

order to complete the reaction some water, a little ether and an excess of precipitated calcium carbonate were added and the whole was warmed under a return condenser on the steam bath. When the iodine had disappeared, the ether was allowed to evaporate and the mixture was distilled in steam. A colorless oil passed over with comparative ease. The latter part of the distillation was very slow and needles formed in the condenser. This proved to be the diiod-*p*-toluidine. On long standing, the oil solidified in the form of long, radiating, colorless prisms. With the above proportions of iodine and *p*-toluidine this substance formed the chief product of the reaction. For example, 25 grams of *p*-toluidine, 54.4 grams iodine, 60 cc. water, 60 cc. ether, and 25 grams calcium carbonate gave, on distilling in steam and then extracting the distillate with ether, 45.5 grams of crude monoiod-*p*-toluidine, or 83.6 per cent. of the calculated.

When this base was distilled with steam, colorless needles separated from the turbid water on standing. These needles, the distillate product, and some material prepared from the pure hydrochloride all melted to a clear oil at 40°. The base is extremely soluble in alcohol, ether, chloroform, benzene, ligroin, or petroleum ether, and it separates from these solvents as an oil. An attempt was made to distil the base under 30 mm. pressure, but when heated decomposition set in, the oil solidified, and only a small portion distilled over. The analytical results obtained in the case of the material melting at 40° were as follows:

	Calculated for C_7H_8NI.	Found.
I	54.50	54.27
N	6.01	5.97

The salts of 3-iod-*p*-toluidine are decomposed by water.

The *hydrochloride*, $C_7H_8NI.HCl$, was prepared by dissolving the base in strong hydrochloric acid at ordinary temperature. The salt separated, on standing, in thick colorless prisms which, when rapidly heated, decomposed with effervescence at 188°. When the strong acid solution was boiled or warmed on the steam bath iodine was liberated. The

salt can be recrystallized, however, by carefully warming in water containing only a little hydrochloric acid.

	Calculated for $C_7H_8NI.HCl$.	Found.
N	5.19	5.11

The *oxalate*, $(C_7H_8NI)_2(COOH)_2$.—A hot alcoholic solution of 3-iod-*p*-toluidine and oxalic acid, when cooled, deposited thick prisms which decomposed at 119°–120°, with effervescence. This salt could be recrystallized from alcohol.

	Calculated for $C_{16}H_{18}O_2N_2I_2$.	Found.
N	5.03	4.87

3-Iod-p-*tolylurea*, $C_7H_6INHCONH_2$.—A nearly quantitative yield of this urea was obtained when a solution of 5 grams of 3-iod-*p*-toluidine in 20 cc. of glacial acetic acid was treated with 3.6 grams of potassium cyanate in 10 cc. of water. The solutions were quickly mixed and kept cool under running water. In a short time a heavy, crystalline precipitate formed. It was filtered and washed with cold water, in which it was nearly insoluble. Hot water or ether dissolved very little. One crystallization from alcohol gave needles; when recrystallized twice more the form had changed to thin, colorless plates, which melted to a clear oil at 187°.

	Calculated for $C_8H_9ON_2I$.	Found.
N	10.14	10.02

3-Iod-p-*acettoluide*, $C_7H_6INHCOCH_3$, from the base and acetic anhydride, was very soluble in alcohol and much less soluble in water. It crystallized from water in needles, having the thickness of a thread and several inches in length, from alcohol in long, colorless prisms, and melted to a clear oil, without effervescence, at 133°.

	Calculated for $C_9H_{10}ONI$.	Found.
N	5.09	5.07

Action of Hydrochloric Acid.—Two grams of 3-iod-*p*-acettoluide were boiled with 20 cc. of concentrated hydrochloric

acid. At first 3-iod-*p*-toluidine hydrochloride (?) separated in a granular cake, but on further boiling this suddenly went into solution. The solution was boiled until faint traces of iodine vapor were noticeable. It was then cooled and the tar which separated was dissolved in acetic acid, precipitated with ammonia, and then crystallized from alcohol. The product formed long, colorless needles melting at 125°. It proved to be 3,5-diiod-*p*-toluidine.

3-Iod-p-*benztoluide*, $C_7H_6INHCOC_6H_5$.—When 3-iod-*p*-toluidine and thiobenzoic acid were mixed, in molecular proportions, and warmed on the steam bath, the liquid produced evolved hydrogen sulphide and then solidified to a mass of crystals. Two recrystallizations from alcohol gave long, colorless needles, which melted without effervescence at 161°.

	Calculated for $C_{14}H_{12}ONI$.	Found.
N	4.15	3.87

Benzenyl-4-amino-3-thiocresol, $C_7H_6\begin{matrix}S\\ \diagup\diagdown\\ N=\end{matrix}CC_6H_5$.—Five grams of 3-iod-*p*-toluidine and 10 grams of potassium thiobenzoate were heated in an oil bath for one and one-half hours at 240°–250°. The cake thus formed was pulverized and thoroughly extracted with hot water. The insoluble material weighed 7.8 grams. It was dissolved in concentrated hydrochloric acid and treated with animal charcoal. The solution then deposited a light yellow, crystalline substance, which melted at 123°–124°. It contained sulphur, and by analysis and the formation of a hydrous platinum double salt it was shown to be identical with the anhydro base obtained by Hess.[1]

	Calculated for $C_{14}H_{11}NS$.	Found.
N	6.22	6.32

The Platinum Double Salt, $(C_{14}H_{11}NS.HCl)_2PtCl_4.H_2O$.—The yellow precipitate produced by platinum chloride in the hydrochloric acid solution of the base was recrystallized from

[1] *Loc. cit.*

dilute hydrochloric acid. It formed yellow needles, which were dried over sulphuric acid.

	Calculated for $C_{28}H_{24}N_2S_2Cl_6Pt.H_2O$.	Found.
H_2O	2.04	2.17
Pt	22.38	21.94

3-Iod-5(?)-nitro-p-acettoluide, $C_7H_6I.NO_2.NHCOCH_3$.—3-Iod-*p*-acettoluide (3.3 grams) was dissolved in nitric acid (26.5 cc., sp. gr. 1.5) cooled with ice water. When all was added the solution was poured upon ice. The precipitate, after washing and drying, weighed 2.8 grams, or 71.7 per cent. of the calculated. It dissolved with difficulty in cold, dilute alkali and was reprecipitated unaltered by hydrochloric acid. For analysis it was purified by crystallizing several times from alcohol. It first formed needles, then prisms, which finally melted at 202°–203°.

	Calculated for $C_9H_9O_3N_2I$.	Found. I.	Found. II.
N	8.75	8.73	8.84

3,5-Diiod-p-toluidine, $C_6H_2\begin{cases}CH_3 & (1)\\ I & (3)\\ I & (5)\\ NH_2 & (4)\end{cases}$.—When *p*-toluidine and iodine were mixed in the proportion of one molecule of the former to two (I_4) of the latter and then warmed, in the presence of ether, water, and calcium carbonate, a little iodine always remained uncombined. With a slight excess of *p*-toluidine the iodine disappeared.

In one preparation, for example, 171 grams of iodine were mixed with 38 grams of *p*-toluidine (the calculated amount being 36 grams). Fifty cc. of ether, an equal volume of water, and 70 grams of precipitated calcium carbonate were added. The mixture was warmed on a return condenser for some time. On distilling in steam it was found that no monoiod-*p*-toluidine came over. The residue in the flask was filtered and extracted by boiling with a liter of alcohol. The solution was allowed to cool, filtered, and the filtrate returned to the flask, and a second extraction was made. After this

operation had been repeated a number of times, about 86 grams of crude, more or less dark, 3,5-diiod-*p*-toluidine was obtained. This is 79 per cent. of the calculated. The final mother liquor contained a black tar. The base can be obtained pure by boiling the alcoholic solution with animal charcoal. It formed, when purified, extremely long, slender needles, melting at 125°, and it agreed with the description of diiod-*p*-toluidine given by Michael and Norton.

3,5-Diiod-p-*acettoluide*, $C_7H_5I_2NHCOCH_3$, from the base and acetic anhydride, by warming on the steam bath, crystallized from alcohol, in thick, colorless prisms which melted at 226°.

	Calculated for $C_9H_9ONI_2$.	Found.
N	3.49	3.46

3,5-Diiodtoluene.—Ten grams of 3,5-diiod-*p*-toluidine were dissolved in 130 cc. of strong alcohol, and 5 cc. of concentrated sulphuric acid were then added. The hot, alcoholic solution was diazotized with powdered sodium nitrite (5 grams), which was added in small portions. After each addition the mixture was boiled until the evolution of nitrogen had nearly ceased. When the product was poured into cold water an emulsion was obtained. This was extracted with ether, the ether evaporated, and the dark-brown oil which remained was distilled in steam. A light yellow oil passed over, which soon solidified to a mass of yellow needles. It weighed 5.75 grams, or about 60 per cent. of the calculated amount. The substance was very soluble in ether, petroleum ether, benzene, and hot alcohol. From alcohol it deposited in bunches of light yellow spikes, which melted at 44.°5–45.°5. It was insoluble in water, acids, or alkali.

	Calculated for $C_7H_6I_2$.	Found.
I	73.83	73.97

3,4,5-Triiodtoluene.—Ten grams of 3,5-diiod-*p*-toluidine were dissolved in 40 cc. of cold, concentrated sulphuric acid and the mixture was diazotized at 0° with 4 grams of powdered sodium nitrite. The solution was allowed to stand for

three hours and was then poured on cracked ice. A little amorphous material was filtered from the cold solution and 18 grams of potassium iodide in 35 cc. of water were added. The black diazo iodide which was formed was warmed on the steam bath until the evolution of gas had ceased and a heavy, black oil lay on the bottom of the flask. When cool, the oil solidified. It weighed 11.5 grams, or 88 per cent. of the calculated. It was insoluble in water, acid, and alkali, but it was fairly soluble in alcohol. Three recrystallizations from alcohol gave long, silky, colorless needles which melted at 122°–123°.

	Calculated for $C_7H_6I_2$.	Found.
I	81.06	80.81

2-Iod-3-nitrotoluene, $C_6H_3\langle^{CH_3\ (1)}_{I\ (2)}_{NO_2\ (3)}$.—3-Nitro-2-aminotoluene was prepared in the manner described by Reverdin and Crépieux.[1] Twenty-seven and one-half grams of this were dissolved in 65 cc. of cold, concentrated sulphuric acid and 18.7 grams of powdered sodium nitrite were added. The mixture was allowed to stand at 0° for four hours and was then poured on ice. An orange-red precipitate formed, but it dissolved almost immediately. It is probable that little or no diazotization took place in the strong sulphuric acid solution but that the nitrous acid acted on the finely divided precipitate when the solution was poured on ice. The cold, pale-yellow solution was treated with 132.5 grams of potassium iodide in 250 cc. of water. The red diazo iodide which formed was decomposed by warming on the steam bath, nitrogen was evolved, and a heavy, black oil separated. A little sodium bisulphite was added and the oil was distilled with steam. A light yellow oil with an aromatic odor easily passed over and finally solidified. From alcohol it crystallized in light yellow plates, which were not at all like the orange-red nitrotoluidine. The plates melted at 67°–68°. The yield was 40.5 grams, or 85 per cent. of the calculated.

[1] Ber. d. chem. Ges., **33**, 2498 (1900).

	Calculated for $C_7H_6O_2NI$.	Found.
N	5.32	5.30

2-Iod-3-aminotoluene.—Fifteen grams of 2-iod-3-nitrotoluene were placed in a one-liter flask with 160 grams of ferrous sulphate. Three hundred cc. of hot water dissolved the ferrous sulphate and melted the nitrotoluidine. Three hundred cc. of concentrated ammonia were added and the flask was closed with a tube provided with a trap. After twenty hours warming on the steam bath the precipitate had become black and had noticeably settled. The mass was then cooled and an attempt was made to distil with steam. Practically nothing came over. The precipitate was filtered and extracted with alcohol and the alcohol was distilled off on the steam bath. The oil that remained now distilled rapidly with steam and even the precipitate which had been extracted with alcohol gave a further quantity of oil. When cooled, the oil solidified. The yield was about 50 per cent. of the calculated. It was purified by dissolving in dilute sulphuric acid and precipitating with ammonia. It was nearly insoluble in water and formed colorless, flat, elongated prisms melting at 41°–42°. It dissolved easily in alcohol and ether and was volatile with these solvents. The hydrochloride and sulphate were difficultly soluble in water. It was dried over sulphuric acid for analysis.

	Calculated for C_7H_8NI.	Found.
N	6.01	5.90

2-Iod-3-acettoluide, prepared from the base and acetic anhydride, was readily soluble in alcohol. From water it crystallized in colorless needles which melted at 135°. It sublimed in long, silky, hairlike crystals.

	Calculated for $C_9H_{10}ONI$.	Found.
N	5.09	5.07

2,3-Diiodtoluene.—Five grams of 2-iod-3-aminotoluene formed a crystalline precipitate, consisting of a difficultly soluble sulphate, when added to a cold mixture of 15 cc. of

concentrated sulphuric acid and 75 cc. of water. The mixture was cooled to 0° and 2.2 grams of powdered sodium nitrite were slowly added. It dissolved almost completely in about two hours, and finally entirely on adding 10 cc. more water. The solution was then added to 17 grams of potassium iodide in 50 cc. of ice water. This produced a bulky, bright red precipitate which, on warming, changed to a heavy, dark oil. This was taken up in ether and filtered from a small amount of red material and an attempt was made to distil in steam, but very little oil passed over. On cooling, the undistilled residue became solid. It was filtered off and crystallized from alcohol by dissolving at ordinary temperature and then cooling in a freezing mixture, as otherwise it separates as an oil. Colorless plates were obtained, which melted at 31°–32°. The melting point was not altered by recrystallizing. When this material was mixed with 3,5-diiodtoluene or 2,5-diiodtoluene the mixture immediately liquefied.

	Calculated for $C_7H_6I_2$.	Found.
I	73.83	74.21

This diiodtoluene is readily soluble in organic solvents.

3-Iod-4-acetaminobenzoic Acid.—Eighteen grams of 3-iod-*p*-acettoluide were suspended in 750 cc. of hot water and 36 grams of magnesium sulphate added. The whole, in a twelve-liter flask, was stirred and kept hot by forcing steam through the mixture. A one per cent. solution of potassium permanganate containing 31.5 grams of the salt was added, slowly at first but more rapidly as the volume of the solution increased. When all of the permanganate had been added the solution was kept hot for one hour and the excess of permanganate was reduced with alcohol. The manganese dioxide was filtered off and washed and the large volume of colorless solution was evaporated to about 600 cc. The solution, when cooled, deposited 0.8 gram of unaltered acetyl compound. When the clear filtrate from this was acidified with hydrochloric acid it gave 13.9 grams of nearly pure acid, or 73 per cent. of the calculated. The

substance was difficultly soluble in hot water and very soluble in hot alcohol or dilute alkali. It formed bunches of needles from water, and long, colorless prisms from alcohol. It melted to a yellow oil at 230°.

	Calculated for $C_9H_8O_3NI$.	Found.
N	4.59	4.55

2-Iod-3-acetaminobenzoic Acid.—This was prepared by oxidizing 2-iod-3-acettoluide with permanganate as above. The proportions used were 6.5 grams of 2-iod-3-acettoluide, 12 grams magnesium sulphate, and 500 cc. of water. To this was added a one per cent. solution of 12 grams of potassium permanganate. Under these conditions the yield was 4 grams, or about 55 per cent. of the calculated. The acid separated from alcohol in needlelike prisms, which melted to a red oil at 199°.

	Calculated for $C_9H_8O_3NI$.	Found.
N	4.59	4.75

3,5-Diiod-4-aminobenzoic Acid.—When the above 3-iod-4-acetaminobenzoic acid was boiled with concentrated hydrochloric acid the main product was not the expected monoiodaminobenzoic acid but, instead, a mixture of 3,5-diiod-4-aminobenzoic acid and *p*-aminobenzoic acid.

Seven and four-tenths grams of 3-iod-4-acetaminobenzoic acid were boiled for several minutes with 50 cc. of concentrated hydrochloric acid. A portion remained insoluble. This material (3.7 grams) was filtered off and it was found that it did not melt at 350°. It was insoluble in water, alcohol and ether. It was purified by dissolving in ammonia and precipitating with acetic acid. This treatment gave minute needles which agreed in properties with the acid obtained by Michael and Norton from iodine monochloride and *p*-aminobenzoic acid.

	Calculated for $C_7H_5O_2NI_2$.	Found.
I	65.29	64.45
N	3.60	3.73

The hydrochloric acid filtrate from the above was evaporated to dryness and the residue taken up in hot ammonium hydroxide. The addition of acetic acid then gave a small amount of diiodamino acid. The filtrate from this was again evaporated to dryness and the residue was crystallized from water. The solution deposited a mixture which consisted mainly of large, brown crystals. These were picked out and recrystallized twice from water. The product was free from iodine and it melted at 185°. It was easily soluble in water, alcohol, and ether. A nitrogen determination gave results agreeing with those calculated for *p*-aminobenzoic acid.

	Calculated for $C_7H_7O_2N$.	Found.
N	10.27	9.94

In order to further identify the above diiodamino acid with that obtained by Michael and Norton, the sodium salt was prepared by dissolving the acid in warm sodium hydroxide. Long, colorless, shining needles separated which, air-dried, gave the following results for water:

0.3343 gram substance lost 0.0602 gram at 160°.

	Calculated for $C_7H_4O_2NI_2Na.5H_2O$.	Found.
H_2O	17.96	18.01

The material therefore agrees in every respect with Michael and Norton's descriptions.

*3,5-Diiod-4-aminobenzoic Acid from 3,5-Diiod-*p*-acettoluide.*—Nine and two-tenths grams of 3,5-diiod-*p*-acettoluide were suspended in 500 cc. of hot water and 12 grams magnesium sulphate were added. Steam was passed in and 11 grams of potassium permanganate were slowly added. When the color of permanganate had disappeared the solution was concentrated and precipitated with hydrochloric acid. The yield of 3,5-diiod-4-aminobenzoic acid was poor, only 1.1 gram being obtained. It was identified by its properties and the following nitrogen determination: Found, 3.42 per cent. nitrogen; calculated, 3.60.

Ethyl Ester of 3,5-Diiod-4-aminobenzoic Acid.—In the

alkylation, with ethyl iodide, of the diiodamino acid the alkyl group might be expected to attach itself to nitrogen. It was found, however, that an ester is formed. Three grams of the potassium salt were dissolved in alcohol and warmed on the steam bath with 3 grams of ethyl iodide for a number of hours. Water was then added and the fine, hairlike needles which were precipitated were found to be insoluble in ammonia. Two crystallizations from strong alcohol gave bunches of long, colorless needles which melted to a yellow oil at 148°.

	Calculated for $C_9H_9O_2NI_2$.	Found.
N	3.35	3.13

3-Iod-4-aminobenzoic Acid.—This acid is the intermediate product in the formation of 3,5-diiod-4-aminobenzoic acid when 3-iod-4-acetaminobenzoic acid is boiled with hydrochloric acid. In one of these experiments the boiling was not as long or as vigorous as usual. When the insoluble portion was dissolved in warm ammonium hydroxide and precipitated with acetic acid a noticeable portion did not separate immediately. The diiodamino acid was filtered off and the filtrate was allowed to stand for some time. It slowly deposited bunches of light-colored, hexagonal prisms which melted at 201°–202°. The material was easily soluble in hot water and alcohol.

	Calculated for $C_7H_6O_2NI$.	Found.
N	5.32	5.20

This acid is best prepared from *p*-aminobenzoic acid and iodine monochloride. If *p*-aminobenzoic acid is dissolved in a small volume of cold hydrochloric acid and one molecular proportion of iodine monochloride in vapor form is passed in, a precipitate forms. This is filtered off but not washed. The crude precipitate is dissolved in ammonium hydroxide and the hot solution made strongly acid with acetic acid. Any diiodamino acid present separates and is filtered off. The filtrate, on standing, deposits light brown prisms of 3-iod-4-aminobenzoic acid. If *p*-aminobenzoic acid is dissolved in a

large amount of dilute hydrochloric acid and one molecular proportion of iodine monochloride is added and the solution warmed or concentrated, 3,5-diiod-4-aminobenzoic acid results.

Action of Iodine upon p-*Aminobenzoic Acid.*—When the potassium salt of *p*-aminobenzoic acid in aqueous solution was treated with two atomic proportions of powdered iodine, a tar was formed which was insoluble in alkali. The compound had therefore lost the carboxyl group. It dissolved in hydrochloric acid, forming a bulky hydrochloride. The aqueous solution of this salt was boiled with animal charcoal and the base precipitated with ammonia. It proved to be *p*-iodaniline. No trace of 3-iod-4-aminobenzoic acid was obtained.

Action of Iodine upon 3,5-Diiod-4-aminobenzoic Acid.—An aqueous solution of 1.7 grams of the potassium salt of 3,5-diiod-4-aminobenzoic acid was boiled with 1.0 gram of powdered iodine. No action was apparent. The mixture was heated in a closed tube at 165° for 5 hours. The tube then contained a black precipitate and some free iodine. The whole was warmed with an excess of dilute potassium hydroxide and filtered. The filtrate gave some unaltered acid on acidifying. The black residue insoluble in alkali was crystallized from acetic acid. This gave brown needles melting at 184°. When mixed with triiodaniline the melting point was not lowered.

3,4-Diiodbenzoic Acid.—One and four-tenths grams of 3-iod-4-aminobenzoic acid were dissolved in 10 cc. of cold concentrated sulphuric acid and 0.7 gram powdered sodium nitrite were added. After standing two hours the mixture was poured on ice and filtered from a trace of impurity. The cold filtrate was treated with 3 grams of potassium iodide in 10 cc. of water and the red precipitate was decomposed by warming. Free iodine was removed by means of sodium bisulphite. The light yellow precipitate, when dry, weighed 2 grams, which is the calculated amount. It was dissolved in ammonia and precipitated by hydrochloric acid and then recrystallized three times from alcohol. It was insoluble in

water, readily soluble in alcohol, and formed arborescent needles melting to a red oil at 257°.

	Calculated for $C_7H_4O_2I_2$.	Found.
I	67.91	68.20

3,5-Diiodbenzoic Acid.—Three and four-tenths grams of 3,5-diiod-4-aminobenzoic acid were dissolved in 15 cc. of cold concentrated sulphuric acid. A large excess (1.5 grams) of powdered sodium nitrite was added and the mixture allowed to stand at 0° for two hours. The diazo solution was poured on ice and a small amount of amorphous material was filtered off. The clear yellow solution thus obtained was added, in small portions, to two volumes of boiling alcohol. When the evolution of gas had ceased the solution was cooled and diluted with considerable water. A white flocculent precipitate (1.35 grams) separated. It was dissolved in dilute sodium hydroxide and precipitated with hydrochloric acid. It was insoluble in water but dissolved easily in alcohol. It was purified by repeatedly dissolving in a few cc. of hot alcohol and pouring into a large volume of boiling water. Finally it was crystallized from 50 per cent. alcohol. It formed slightly yellow prisms, which melted to a red oil at 235°. When this was mixed with a sample of 3,5-diiodbenzoic acid prepared from 3,5-dinitrobenzoic acid the melting point was not lowered. A halogen determination gave:

	Calculated for $C_7H_4O_2I_2$.	Found.
I	67.91	68.18

3,4,5-Triiodbenzoic Acid.—Three and eight-tenths grams of 3,5-diiod-4-aminobenzoic acid were diazotized in the manner described above. When the cold diazo solution was treated with a solution of 9 grams of potassium iodide in 20 cc. of water it gave a dark red precipitate. The mixture was warmed on the steam bath until the evolution of nitrogen ceased, and the free iodine was removed with a little sodium bisulphite. The light yellow precipitate weighed 3.6 grams, or 72 per cent. of the calculated. The acid was dissolved in

ammonium hydroxide and precipitated with acetic acid. It was then crystallized three times from strong alcohol. It is easily soluble in alcohol and alkali and insoluble in water and acids. It formed bundles of needlelike prisms which melted to a red oil at 288°.

	Calculated for $C_7H_3O_2I_3$.	Found.
I	76.20	76.41

The sodium salt, $C_6H_2O_2I_3Na.2\frac{1}{2}H_2O$, prepared from the acid and sodium hydroxide, formed long, colorless needles, which were only moderately soluble in water. The salt was dried in the air and the water of crystallization was determined.

0.4642 gram salt lost 0.0367 gram at 150°.

	Calculated for $C_7H_2O_2I_3Na.2\frac{1}{2}H_2O$.	Found.
H_2O	7.93	7.90

3,5-Diiod-4-oxybenzoic Acid.—Six grams of 3,5-diiod-4-aminobenzoic acid were dissolved in 25 cc. of cold concentrated sulphuric acid and 3 grams of powdered sodium nitrite were added. After standing four hours the mixture was poured on ice and filtered. The yellow diazo solution was allowed to stand for some time and then warmed on the steam bath. A light yellow precipitate formed which weighed 5.4 grams, or 90 per cent. of the calculated. The substance was easily soluble in alkali and alcohol but insoluble in water. It was dissolved in dilute alkali, treated with animal charcoal, and precipitated with dilute hydrochloric acid. The material was dissolved in alcohol and precipitated with water, and this operation was repeated several times, but it still contained some impurity. Finally it was converted into the methyl ester, as described below, which, as Auwers and Reis[1] have shown, forms needles and melts at 167°. From the pure ester the acid was obtained by saponification. When it was then crystallized from alcohol it agreed in all particulars with Peltzer's diiod-*p*-hydroxybenzoic acid, obtained by direct

[1] Ber. d. chem. Ges., **29**, 2360 (1896).

iodation of *p*-hydroxybenzoic acid. When heated it gave off iodine above 220° and decomposed with effervescence at about 260°. This melting point was not lowered when the substance was mixed with Peltzer's diiod-*p*-hydroxybenzoic acid, prepared by direct iodation.

	Calculated for $C_7H_4O_3I_2$.	Found.
I	65.13	64.43

The following experimental work was done by Dr. S. H. Clapp: He found that the above 3,5-diiod-4-hydroxybenzoic acid could be most conveniently prepared by dissolving *p*-hydroxybenzoic acid in water containing four molecular proportions of potassium hydroxide and then adding the calculated quantity of powdered iodine. The action took place with evolution of heat, the solution darkened, and at times the diiod acid separated before the addition of iodine was completed. In the latter case, dilute alkali was added and the addition of iodine continued. The clear solution was acidified with hydrochloric acid and the precipitate, after filtering, was boiled with water to remove any unaltered acid. It was then crystallized by dissolving in hot alcohol and precipitating with hot water. The yield of pure diiod acid was 80 to 87 per cent. of the calculated.

Methyl Ester of 3,5-Diiod-4-hydroxybenzoic Acid.—Three grams of the acid were boiled in 75 cc. of methyl alcohol with 5 drops of concentrated sulphuric acid. After three or four hours the solution was cooled, whereupon the ester separated in long, snow-white, prismatic needles. The yield was 90 per cent. of the calculated. It was practically insoluble in water but readily soluble in dilute sodium hydroxide and in alcohol. On crystallizing from alcohol it melted constantly at 166°–167°.

	Calculated for $C_8H_6O_3I_2$.	Found.
I	62.87	63.33

Methylation of 3,5-Diiod-4-hydroxybenzoic Acid.—The dipotassium salt of 3,5-diiod-4-hydroxybenzoic acid, prepared by dissolving 30 grams of the acid in water containing 11 grams of

potassium carbonate and evaporating to dryness, was dissolved in alcohol and 40 grams of methyl iodide were added. The mixture was boiled, under a return condenser, for 5 hours, although the reaction seemed to be complete in a much shorter time. The solution was filtered from potassium iodide and evaporated to dryness. The residue was stirred with water, filtered, and then digested with dilute sodium hydroxide. The material remaining insoluble weighed 24.0 grams, or 75 per cent. of the calculated for the methyl ester of 3,5-diiod-*p*-anisic acid, $CH_3OC_6H_2I_2COOCH_3$. This ester crystallized from alcohol in long, snow-white prisms melting at 95°.

	Calculated for $C_9H_8O_3I_2$.	Found. I.	II.
I	60.77	61.01	60.74

The alkaline solution mentioned above was acidified, whereupon 4.2 grams of 3,5-diiod-*p*-anisic acid, $CH_3OC_6H_2I_2COOH$, were obtained. The same acid was obtained when the above methyl ester was warmed with dilute sodium hydroxide.

*3,5-Diiod-*p*-anisic acid* crystallizes from alcohol in colorless needlelike prisms. When heated it shows signs of change at about 220° and decomposes to a red oil at 255°–256°.

	Calculated for $C_8H_6O_3I_2$.	Found.
I	62.87	62.73

p-Hydroxybenzoic acid gives a yellow precipitate or coloration in aqueous solution with ferric chloride. 3,5-Diiod-*p*-hydroxybenzoic acid and its methyl ester give no color in the cold; on boiling with ferric chloride a red color is produced.

NEW HAVEN, CONN.,
May, 1909.

LEAD SILICATES:
THERMAL ANALYSIS OF THE SYSTEM PbO–SiO_2.

BY H. C. COOPER, L. I. SHAW AND N. E. LOOMIS.[1]

"Lead silicates" are such characteristic glasses that in the light of modern physico-chemical studies they are much more

[1] Reports on parts of this work were submitted to Syracuse University by Messrs. Shaw and Loomis in candidacy for the Master's degree.

properly regarded as solutions than as definite substances. The various formulae occurring in works on metallurgy and glass manufacture, in which arts "lead silicates" are of considerable importance, are, therefore, without precise meaning. It is known, however, that glass tends to crystallize when cooled too slowly and Vogt[1] reports with some uncertainty having seen incidentally some synthetic $PbSiO_3$ in the laboratory of L. Bourgeois (Paris, 1885) which was optically uniaxial and positive with feeble interference colors.

Of more significance are the crystallized masses which are occasionally found under the fusion hearth of a dismantled lead roasting furnace. Through the courtesy of Mr. F. L. Graves, we are in possession of some specimens bearing crystals several millimeters in diameter. Analyses given by Dana and Penfield[2] and by H. A. Wheeler[3] point to the formula $7PbO : 4SiO_2$. Equally interesting is the mineral barysilite[4] reported from Sweden by A. Sjögren and C. H. Lundstrom, in 1888. Specimens are much like the metallurgical by-products aforementioned and have a similar composition, $3PbO : 2SiO_2$ being the nearest empirical formula of simple ratio.

After the present research had been planned, Wl. Mostowitsch[5] published a careful investigation of the cooling curves of PbO–SiO_2 mixtures. He observed the separation of lead oxide from solutions containing an excess of that component and noted the gradual lowering of the freezing point as the silica increased, but for most of the mixtures the undercooling was very great and the heat effects were conspicuous; there was no noticeable regularity in the freezing points. All of his cooled products seem to have been amorphous, either vitreous or "waxlike," and his conclusion was that the lead silicates are solutions of lead oxide in lead glass.

Methods of Study.—We proposed to study the heating curves instead of the cooling curves, provided the mixtures could be got to crystallize. Fortunately we succeeded in

[1] Die Silikatschmelzlösungen, Christiania, 1903, **1**, 45.
[2] Dana and Penfield: Am. J. Sci., [3] **30**, 138 (1885).
[3] H. A. Wheeler: *Ibid.*, [3] **32**, 272 (1886).
[4] See Dana: System of Mineralogy.
[5] Metallurgie, **4**, 647 (1907).

preparing a long series of crystallized mixtures. In developing the methods of study we were very substantially aided by the recent work of the Geophysical Laboratory on the calcium and magnesium silicates[1] and by numerous suggestions from members of its staff.

A small Hoskins electric resistance *furnace*, insulated by an extra outer fire-clay cylinder, served admirably for the work, which was at temperatures below 900°. The melting points were at first taken in 5 cc. *crucibles*, but were subsequently taken in still smaller cylinders, or capsules, of pure platinum supported directly by the platinum-tipped porcelain tube, protecting the thermocouple (see p. 464). The temperature was easily regulated with the aid of a board of thirty incandescent lamps. A *thermo-element* with potentiometer installation was used to measure the temperature. Three thermo-elements (Pt *vs.* Pt–Rh) were furnished from the same batch (XY) of wire by the Cambridge Scientific Instrument Co., Ltd., the batch having been tested by the National Physical Laboratory (1908) up to 1300° and values assigned. The temperatures given below are based on these values. We hope shortly to be equipped for the calibration by metal melting points according to the Reichsanstalt. The temperatures can then be corrected, if necessary, without difficulty, since the melting points of the pure compounds are sufficiently constant. One of our couples remained unused, the other has been used exclusively to measure the temperature of the furnace interior, while the third has been immersed naked in the lead silicate melts. After a year's use the couple that has been used in the melts does not materially differ in thermo-electric effect from the furnace couple. The former was cleaned each time after using by dipping in hot dilute nitric acid, washing and polishing. This couple, as well as the other platinum objects in contact with the silicate, was examined with a lens regularly before being used.

The couple wires were insulated by slender tubes of Marquardt porcelain and supported by a larger encasing tube of

[1] Allen, White and Wright: Am. J. Sci., [4] **21**, 89 (1906). Allen, Wright and Clement: *Ibid.*, [4] **22**, 385 (1906). Allen, White, Wright and Larsen: *Ibid.*, [4] **27**, 1 (1909).

similar material. This larger tube was continued at the lower end by a short platinum tube, to which the capsule could be attached. No current leakage effects were apparent. The cold-junction bath was at zero temperature.

The *potentiometer* was a simple instrument specially designed for this work by Dr. W. P. White, of the Geophysical Laboratory, and made by the Leeds and Northrup Company. It is provided with the proper resistance for use with a Weston Standard Cell and contains three sets of resistances and the corresponding dials, the first reading millivolts, the second tenths, and the third hundredths, of millivolts. The thousandths, or microvolts (and, in practice, usually also the hundredths of millivolts), are read from the galvanometer.

The *galvanometer* used was Leeds and Northrup's High Sensibility Galvanometer No. 2280, modified to afford a period of less than five seconds. It was mounted at such a distance from the telescope that a deflection of 20 cm. corresponded to one-tenth millivolt. The scale was renumbered to read microvolts directly. At 700° a deflection of 1 mm., which could be conveniently detected, corresponded to about one-twentieth degree. It is probable, however, that the *accuracy of the work* as a whole was limited to whole degrees. A shunt switch containing resistances to reduce the galvanometer deflection to one-tenth was of assistance as a "coarse adjustment" in using the sensitive galvanometer. Commutators of the mercury-cup type were provided for exchanging the connections of the two couples and also for putting the normal cell in circuit. The installation was sufficiently convenient for readings to be taken at quarter-minute intervals or oftener. In practice the furnace couple was read at one quarter, and the melt couple at the other three quarters, of the minute. In addition the normal cell was balanced every 5–8 minutes.

For the heating-effect determinations the capsules were filled regularly to a constant height and contained each time about six grams of the (unusually dense) mixture. The couple was always immersed to the same depth and the capsule lowered to a constant depth in the furnace chamber.

Preparation of the Substances.—It is not so easy to purify *lead oxide* as certain other lead compounds from which lead oxide is readily obtained. Following Faraday's[1] example, we used lead nitrate, purifying it by the method of Baekeland.[2] According to his determinations the nitrate is completely converted into the oxide by heating to about 357°. We could detect no nitrous compounds in our lead oxide so prepared. In an analysis of our purified lead nitrate 0.8470 gram $Pb(NO_3)_2$ gave 0.7755 gram $PbSO_4$, instead of 0.7754 gram calculated.

The *silica* used for the measurements given below was a pulverized quartz several times purified by Baker and Adamson, under the attention of Mr. G. P. Adamson. On evaporation with hydrofluoric acid 1.0459 grams quartz left a residue of 0.0005 gram (corrected for acid residue). Before weighing, the silica was ignited in a platinum crucible over a blast lamp for fifteen minutes, which was found to reduce it to constant weight.

In making the *various mixtures* the lead nitrate was added to the silica directly; the mixture was then stirred and slowly heated in a loosely covered platinum crucible in the electric furnace. After the evolution of the nitrous fumes (with almost no spattering) the mixture was heated to quiet fusion; then the crucible was given a circular motion with the tongs, replaced and allowed to cool. The solidified melt was powdered in an agate mortar, reheated in a small crucible, cooled very slowly, ground to pass through an 80-mesh sieve, and returned to the crucible. The mixture was then heated for periods of several hours at temperatures 10°–100° below the approximately known melting point. After the sintered mass had cooled with the furnace it was again put through the 80-mesh sieve, with the help of more or less grinding, and transferred to the capsule for a melting point determination. The series of mixtures was prepared on a stoichiometric basis, the percentage compositions being based on the

[1] M. Faraday: Trans. Roy. Soc., **1830**, 1.
[2] L. Baekeland: Dissociation of $Pb(NO_3)_2$, J. Am. Chem. Soc., **26**, 391 (1904).

equivalent weights[1] and care being taken to include the mixtures of simple ratios. We succeeded in crystallizing a melt containing as little as 43 equivalent per cent. PbO; this is the present limit of the series. The 48 per cent. mixture was rather slow to crystallize, while the 43 per cent. mixture crystallized only after inoculation with (an analytically negligible quantity of) the 50 per cent. substance. The difficulties involved in crystallizing the more siliceous solutions may perhaps later be obviated, but they seem at present to be disproportionately greater than the likelihood of finding interesting phenomena. The work of preparation of the mixtures is partially summarized in the table given below (p. 470).

All of the mixtures crystallized upon sintering. In case of rapid cooling of the melt those mixtures containing less than 80 equivalent per cent. PbO formed colored glasses. The manner of cooling affects the physical appearance surprisingly, even when crystalline. Lead oxide itself was incidentally obtained from lead nitrate in five forms decidedly different to the eye, *viz.*, yellow powder, reddish-brown powder, copper-colored granular material, small green lustrous flakes, large copper-colored flakes. R. Ruer reports[2] that lead oxide has two modifications with a transition point at 500°–600°. We shall again refer to this in connection with the consideration of eutectic points.

The Measurements of the Heating Effects.—Preliminary experiments were made with a series of mixtures on a slowly heated platinum ribbon (modified Joly Meldometer) after the manner of Day and Shepherd,[3] but the confusing irregularity in the order of melting, immaterial whether powder or fragments were used, prevents us from sharing their enthusiasm for the method.

Cooling curves for a few of the melts were measured in the

[1] It seems regrettable that the compositions of such series should ever be given on a simple weight per cent. basis. A series containing a very dense substance like PbO well illustrates the difficulty imposed on the reader by such a basis. There would have to be a recalculation according to the combining weights before the combining ratios could be ascertained. $PbSiO_3$, for instance, contains 79 weight per cent. PbO.

[2] Z. anorg. Chem., **50**, 265 (1906).

[3] J. Am. Chem. Soc., **28**, 1101; Am. J. Sci., [4] **22**, 265 (1906).

fore part of the work, but, like Mostowitsch,[1] we observed little of interest, except the points of first separation out of lead oxide and the marked undercoolings. Messrs. Allen and White[2] have called attention to the unreliability of cooling curves in the study of high melting points (see below on the melting point of lead oxide).

The heating curves were similar in general form to the cooling curves of easily crystallizing substances, showing an extended, nearly level portion at the melting point of the pure substance; in the case of the intermediate mixtures we had very little difficulty in detecting the breaks for both eutectic melting and final dissolving of the excess component. The simultaneous furnace curve[3] was taken in each case, some typical diagrams being seen below (see Fig. II.). Not only does the furnace curve enable one to detect fluctuations due to irregular current supply or control of the same, but it shows the sudden rise of furnace temperature immediately following the principal melting phenomenon. In the cases of definite compounds the temperature, instead of remaining strictly constant during melting, underwent a gradual, very slow rise, generally slowest at the end of the melting. The lack of sharpness of the melting point is similar to that observed by Allen and White,[4] the total heat absorption covering only about 10°, however, and the strongest heat absorption being, for the pure compounds, at the upper three degrees. For the sake of uniformity, the highest temperature of strong absorption was taken as the melting point.

Melting Point of Lead Oxide.—We find this to be 888°. The diagram (Fig. I.), representing a single run of two heatings and two coolings, is very instructive in that it illustrates the unreliability of cooling curves and throws some light on the selection of the proper melting point. In the first heating curve, heat absorption begins at 870° and increases up to 889°.5, about which point the temperature oscillates for a

[1] Metallurgie, **4**, 647 (1907).

[2] Am. J. Sci., [4] **27**, 3 (1909).

[3] See G. K. Burgess: "Methods of Obtaining Cooling Curves," Bull. Bur. Stand., **5**, 199, or Electrochem. Met. Ind., **6**, 366, 373 (1908).

[4] Am. J. Sci., [4] **27**, 6 (1909).

half-minute before jumping upward. In the succeeding cooling the undercooling proceeded steadily to 855°.5, when the unstable liquid released itself, and the next and highest temperature to be noted was 881°. A minute later the temperature remained constant nearly two minutes at 876°, whereupon the mixture ceased to evolve heat and its temperature dropped rapidly to the furnace temperature. The next heating curve, taken without removing the couple from the melt just crys-

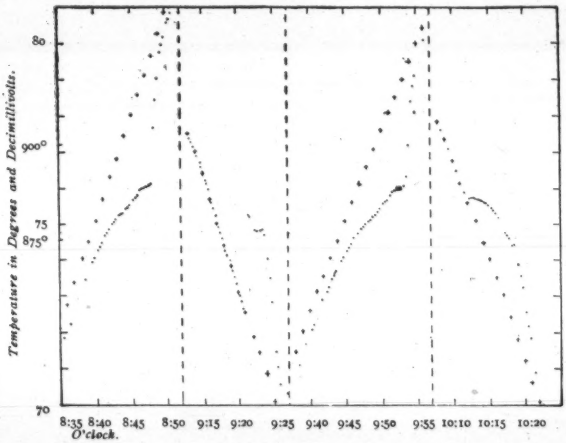


Fig. 1.—Successive heating and cooling curves of lead oxide (single experiment).

+ + + Furnace; · · · · Substance.

tallized (the first heating curve was made after the substance had crystallized and been ground), shows a beginning of absorption again at about 870°, whereupon the temperature rose steadily, fluctuated for a minute between 887°.5 and 889°, came to rest for half a minute at the lower temperature, and then rose very rapidly to the furnace temperature. The succeeding cooling curve is of interest, because, for whatever

reason, there was evidently less than half a degree of undercooling, the freezing temperature remaining constant for a minute at 885°.5, whereupon it fell at a slowly increasing rate through fifteen degrees and then dropped suddenly. While the former cooling curve shows the serious error (in this case nearly ten degrees) liable to result from relying on cooling curves, even when silica and silicates are absent (an ordinary thermocouple galvanometer might have allowed one to catch a higher maximum than the somewhat clumsy potentiometer and sensitive galvanometer, but accuracy would have to be sacrificed), the last, accidentally favorable curve affords a good determination of the freezing point and deserves comparison with the breaks in the heating curves as a reliable determination of the equilibrium point. The true melting point cannot be lower than the maximum of the last cooling curve, which is within about three degrees of the (practically constant) maximum of the heating curves. We seem justified, therefore, in taking the maximum of the heating curve as the melting point, in spite of the fact that the reason for the heat absorption beginning at a much lower temperature can only be guessed at.

The following table gives various data and observations concerning the preparation of the mixtures and the transformation points (eutectic and final melting) as determined from the various heating curves. In the cases of the more significant mixtures two or more determinations were made and the mean is given. The double data for the eutectic points in the cases of the higher mixtures are discussed below under "eutectic points."

Equivalent per cent. PbO.	Ratio PbO : SiO_2.	Result of slow cooling of melt.	Sintered at a furnace temperature of	Eutectic point.	Melting point.
100.0					888
90.00	9 : 1	Dark gray crystalline mass with large bright yellow patches of crystals	860 → 680	720; 727	853
87.00	....	Coarsely crystalline	712, then 690	722; 729	825
80.00	4 : 1	" "	723 → 680	(723)	(723)
77.78	7 : 2	Crystalline	712, then 690	718	727
75.00	3 : 1	"	713 → 680	(716)	(716)
71.43	5 : 2	"	713 → 680	718	732
69.00	....	"	738 → 680	714	742
66.67	2 : 1	"	723 → 680	...	746
65.00	....	"	738 → 680	717	742
60.00	3 : 2	"	712, then 690	718	722
57.14	4 : 3	Upper half vitreous, lower crystalline	713 → 680	716	723
52.00	....	Smoky glass with crystal nuclei	753 → 680	718	764
50.00	1 : 1	Amber glass with crystal nuclei	753 → 680	...	766
48.00	....	Pale yellow glass with crystal nuclei	753 → 680	...	765
42.86	3 : 4	Almost colorless glass, with crystal nuclei(?)	743 → 690	...	760

A good idea of the different types of heating curves can be had from Fig. II., in which a group of actual heating curves centering about the orthosilicate ($2PbO : SiO_2$) is reproduced. The curves for 65 and 69 per cent. are very similar, the melting point of the solution, as well as the eutectic point, being well defined. In the 71.4 per cent. (5 : 2) curve the eutectic melting is the preponderant effect, while in the 66.67 per cent. (2 : 1) curve we observe only the melting effect of the pure compound.

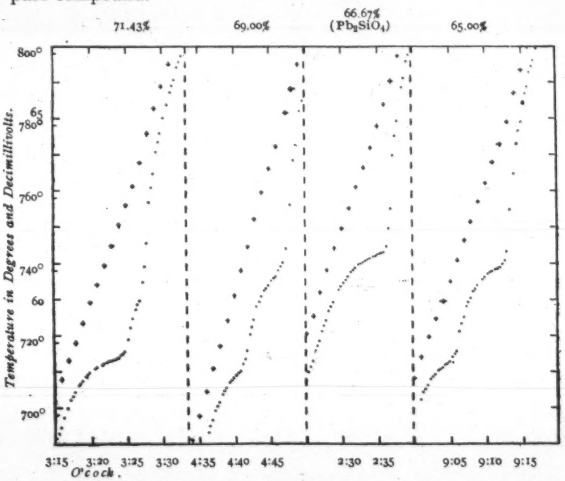


Fig. 2.—Typical heating curves arranged in series according to equivalent percentage PbO.

Equilibrium Curve.—All of the significant points are represented graphically in the melting point curve of the system, as shown in Fig. III. The maxima for the orthosilicate, Pb_2SiO_4, and metasilicate, $PbSiO_3$, leave little to be desired for sharpness.

Eutectic Points.—The eutectic point for solutions of the two silicates may be taken as 717°. The eutectic point for PbO–

Pb_2SiO_4 solutions is confused by another well-marked effect, presumably a crystallographic inversion point, which is so close to the eutectic point that neither can be definitely fixed without further microscopic study. It is not unlikely that the allotropy of lead oxide mentioned above (p. 466) is the

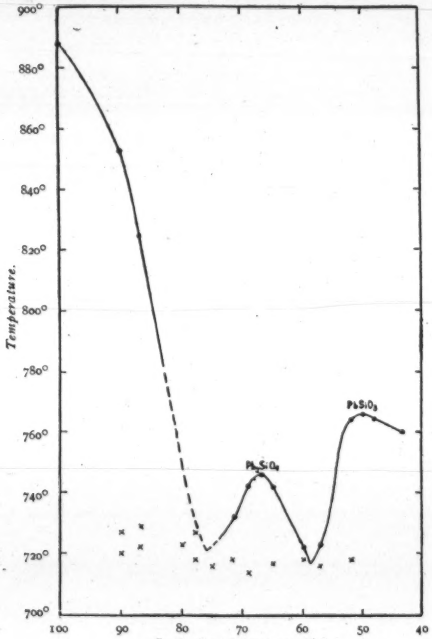


Fig. 3.—Melting point curve.

cause of the confusion. On account of this uncertainty the portion of the curve adjacent to this eutectic point is of a provisional nature.

Crystallographic Observations.—Both of the silicates dis-

covered crystallize readily under suitable conditions, described above. Microscopic measurements have shown the orthosilicate crystals to be hexagonal. They are very similar to the laminar crystals found in specimens of barysilite from Langbanshyttan, Sweden. We are planning to continue the optical studies in connection with further thermal observations. An attempt will be made to recrystallize the lead silicates from a high-temperature solvent.

The thermal analysis would indicate that the mineral barysilite and the metallurgical "lead silicate" approximate the eutectic mixture, but contain an excess of the orthosilicate. The occurrence of small single crystals scattered through the dark brown or gray mass in nearly all the specimens would confirm this inference. The optical study should be of great assistance in this connection.

Industrial Application.—The principal metallurgical value of this investigation is that it shows the existence of definite compounds which presumably participate in the processes of treating lead ores. In the glass industry the only commercial glass known to us which falls within the series studied is the "heaviest flint glass"[1] with 78 weight per cent. (49 equivalent per cent.) of lead oxide and the rest silica. Such glass undoubtedly tends to crystallize in the factory on slow cooling, for it is very close to the composition of the crystallizable silicate, $PbSiO_3$.

Summary.—A large number of mixtures of lead oxide and silica, prepared in series, have been obtained crystalline by slow cooling of the melt and the heating curves have been studied. The resulting well-defined curve of melting points shows maxima for the orthosilicate and metasilicate (Pb_2SiO_4 and $PbSiO_3$). Some significant melting points given are: PbO, 888°; Pb_2SiO_4, 746°; $PbSiO_3$, 766°; eutectic Pb_2SiO_4–$PbSiO_3$, 717°.

SYRACUSE UNIVERSITY,
August 25, 1909.

[1] Made by Schott u. Gen., Catalog Type S. 57.

OBITUARY.

SAMUEL WILLIAM JOHNSON.

Professor Johnson, whose death, after a brief illness, at his home in New Haven was announced July 21st, was born in Kingsboro, New York, on July 3, 1830. His boyhood was spent on the large farm of his father, a retired business man, and it was doubtless from him that the boy acquired his interest in those agricultural problems to which he devoted so large a part of his life. From his tenth to his seventeenth year he studied at Lowville Academy where he obtained his first knowledge of chemistry from Professor David Porter Mayhew, whose assistant he became. While there in 1847, he published his first paper, "On Fixing Ammonia."

In 1848, he fitted up a laboratory of his own, making most of his reagents himself. After teaching three years, he was able to enter Yale in 1850 and studied under Norton and Silliman. In 1853, he went to Europe and worked in the laboratories of Erdmann, Liebig, Kobel and Pettenkofer and for a short time with Frankland in England. He also attended some of the lectures of Chevreul in Paris.

He returned to Yale in 1855 as chief assistant in the Scientific School. The following year he was made professor of analytical chemistry, and in 1857 succeeded Porter in the chair of agricultural chemistry, which he occupied until 1875. He was then appointed professor of agricultural and theoretical chemistry and he continued to teach these subjects, as well as organic chemistry, until his retirement in 1895.

Even from his student days Professor Johnson had taken an active interest in agricultural chemistry and in 1866 became a member of the first Connecticut State Board of Agriculture. It was very largely through his efforts that an act was finally passed in 1877 establishing an agricultural experiment station, the first on the continent.

He very early became a member of the American Association for the Advancement of Science, and in 1866 was elected to the National Academy of Sciences. He was long affiliated with the American Chemical Society, serving as its president in 1878. He was also one of the original members of the American Association of Official Agricultural Chemists and its president in 1888.

His books, "How Crops Grow" and "How Crops Feed,"

have been translated into half a dozen foreign languages and are the most widely read and studied books of their kind in the world. His translations of Fresenius' "Qualitative and Quantitative Analysis" are also familiar to American college students. His other publications number fifty or more papers, mostly on purely chemical subjects, although some bear on mineralogy.

REVIEWS.

DIE CHEMISCHE INDUSTRIE. Von GUSTAV MÜLLER, Kaiserl. geheimer Oberregierungrat, Vortr. Rat im Reichsamt des Innern. Unter Mitwirkung von DR. PHIL. FRITZ BENNIGSON, bei den Konigl. Techn. Instituten der Artillerie. Leipzig. B. G. TEUBNER, 1909. Price, M. 11.20.

This is one of the most recent volumes in this valuable series. It deals chiefly with the commercial side of chemical industry. The chief topics are statistics of production in Germany and other countries; German internal revenue and import and export duties; German laws applying to manufacture, to storage and to the care and protection of the workman in the various industries; number of workmen employed in a given industry, their age, sex and average wage; variations in price and average dividends of an industry; syndicates of manufacturers or dealers. The chemical data given are good and clear but brief, indicating methods of manufacture and including brief historical data, but avoiding detail.

This is a thorough and useful book; while it is chiefly valuable to the merchant and the manufacturer, it contains enough of interest to a chemist to repay perusal. E. R.

A COURSE IN INORGANIC CHEMISTRY FOR COLLEGES. By LYMAN C. NEWELL, Ph.D. (Johns Hopkins), Professor of Chemistry, Boston University. Boston: D. C. Heath and Co., 1909. pp. 594. Price, $2.

This book is intended for college students who devote a year to general chemistry. It contains as much matter as can be clearly handled in a book of the size, and the treatment is clear throughout. The electrolytic dissociation theory is introduced to explain the phenomena of neutralization, and other theoretical subjects receive clear though necessarily brief illustration. More reference is made to chemical industry than is common in books of this size. The book is illustrated by portraits of Dewar, Ramsay, Madame Curie and others. On the whole, this is a very excellent college manual. E. R.

AN INTERMEDIATE COURSE OF LABORATORY WORK IN CHEMISTRY. By EDWARD KENNETH HANSON, M.A., and JOHN WALLIS DODGSON, B.Sc. London and New York: Longmans, Green and Co. pp. 124.

This book is written to prepare students for the London Intermediate Science Examinations, and is chiefly given to well-selected and illustrated inorganic and organic preparations, and to excellent treatises on volumetric and gravimetric analysis, while the closing twenty-five pages explain just enough of qualitative analysis to enable a student to analyze simple salts, but not to analyze mixtures or minerals.

The book is well written, but can have little vogue in this country, as we always teach qualitative analysis before preparations or serious quantitative work. It may be that we are wrong; it may be urged that the setting-up and manipulation of apparatus involved in preparations, and the neatness and accuracy required for quantitative work fit a student for qualitative work, while teachers know that beginners may analyze correctly but yet develop slovenly ways hard to eradicate, and fatal to satisfactory quantitative or preparative work.

E. R.

TABLES OF PROPERTIES OF OVER FIFTEEN HUNDRED COMMON INORGANIC SUBSTANCES. By WILHELM SEGERBLOM, A.B., Instructor in Chemistry at the Phillips Exeter Academy. Exeter, N. H.: Exeter Book Publishing Co. pp. 144.

These tables give the principal properties of such substances as may reasonably be looked for in a course of qualitative analysis. The author acknowledges his indebtedness to Watts, Dammer, Comey and others, references without which, indeed, the book could not have been written. Quantitative statements of solubilities instead of the mere statements soluble or insoluble in water would add to the value of the book without increasing its volume. Mr. Segerblom's compilation should be welcomed as a ready reference book for every day in school, college and commercial laboratories.

E. R.